User's guide for RetrasoCodeBright (RCB)

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1. Introduction

The code RetrasoCodeBright (RCB) is designed to model complex problems consisting of coupled thermic, hydraulic and geochemical processes. It has the following features:
- Simulation of the flow of liquid and/or gas in a multi-phase approach.
- Simulation of heat transport.
- Condensation and evaporation of water with their effects on the heat transport.
- Simulation of meteorological phenomena as boundary conditions.
- Simulation of transport (advection, dispersion and diffusion) of chemical species in the liquid and gas phase.
- Simulation of the following chemical reactions: aqueous complexation (including redox and acid-base reactions), sorption (including cation exchange) by means of electrostatic or non electrostatic models, precipitation and dissolution of minerals and gas liquid interaction. Precipitation and dissolution can be considered kinetically or in equilibrium. The other reactions are always assumed in equilibrium.
- Effects of precipitation and dissolution on porosity and permeability.
- Effects of aqueous solutes on certain flow properties.
- The code can use one, two and three dimensional finite elements for its spatial discretisation.
- A user friendly interface can be used for pre and post-processing.

RCB is the result of coupling two codes: CodeBright and Retraso. CodeBright (COupled DEformormation of BRIne Gas and Heat Transport) was designed for the thermo-hydraulic-mechanical analysis of three-dimensional multiphase saline media (Olivella et al., 1996; Departamento de Ingeniería del Terreno, 2002). Retraso (REactive TRAnsport of SOlutes) is a code for solving two-dimensional reactive transport problems (Saaltink et al., 1997). Basically, in the coupled code RCB, a CodeBright module calculates the flow properties (Darcy flux of liquid and/or gas, saturation, temperature, density, etc.) and passes it to a Retraso module for the calculation of reactive transport. RCB models the features of both codes except the solution of the mechanical problem (deformation). Therefore, the mechanical part will not be treated in this user's guide.

This user's guide starts by giving a mathematical description of all modelled processes. As RCB includes the modelling of many thermohydraulic processes, a list of all thermohydraulic constitutive laws and parameters that describe these processes is given in chapter 3. In chapter 4 all input and output files are described. RCB also includes a user friendly interface for pre and post-processing. In stead of explaining all the details of this interface, we opted for giving a tutorial for a modelling a simple case. This is done in chapter 5.

2. Processes and governing equations

2.1. Thermohydraulic processes

RCB formulates the flow problem in a multiphase approach, that is, a porous media composed of solid grains, water and gas. Within this porous media, thermal and hydraulic aspects will be taken into account, interacting simultaneously and considered in an integrated way. Three phases are considered: solid phase (mineral), liquid phase (water and dissolved air), gas phase (mixture of dry air and water vapour). Three components are considered: water, dry air and heat. Mass balance equations are formulated for each component. To each mass balance a state variable is associated: liquid pressure (P_l in MPa), gas pressure (P_g in MPa) and temperature (T in ^{0}C). Constitutive laws have to be used to express the mass balance equations as function of the state variables.

2.1.1. Mass balances

The total mass balance of water is expressed as:

$$\frac{\partial}{\partial t}\left(\omega_l^w \rho_l S_l \phi + \omega_g^w \rho_g S_g \phi\right) + \nabla \cdot \left(\mathbf{j}_l^w + \mathbf{j}_g^w\right) = f^w \tag{1}$$

where subscripts l and g refer to liquid and gas and superscript w to water, ω is the mass fraction (kg kg^{-1}) of a component in a phase, ρ is the density (kg m-3) of a phase, S is the hydraulic saturation (m^3 m^{-3}), ϕ is the porosity (m^3 m^{-3}), $\mathbf{j}$ (kg m^{-2} s^{-1}) is the total flux (advective, dispersive and diffusive) and f is an external source/sink term (kg m^{-3} s^{-1}). Note, that the first term represents the change of mass of water in the liquid phase, the second term represents the change of mass of water in the gas phase (i.e., vapour) and the third and fourth terms represent the transport of water in liquid and the gas phase, respectively.

Similar to the mass balance of water, the mass balance of air can be expressed as:

$$\frac{\partial}{\partial t}\left(\omega_l^a \rho_l S_l \phi + \omega_g^a \rho_g S_g \phi\right) + \nabla \cdot \left(\mathbf{j}_l^a + \mathbf{j}_g^a\right) = f^a \tag{2}$$

where superscript a refers to air.

The equation for internal energy balance for the porous medium is established taking into account the internal energy in each phase (E_s, E_l, E_g in J kg^{-1}):

$$\frac{\partial}{\partial t}\left(E_s\rho_s(1-\phi)+E_l\rho_l S_l\phi+E_g\rho_g S_g\phi\right)+\nabla\cdot(\mathbf{i}_c+\mathbf{j}_{Es}+\mathbf{j}_{El}+\mathbf{j}_{Eg})=f^Q \tag{3}$$

where $\mathbf{i}_c$ is energy flux (J m^{-2} s^{-1}) due to conduction through the porous medium, the other fluxes ($\mathbf{j}_{Es}$, $\mathbf{j}_{El}$, $\mathbf{j}_{Eg}$) are advective fluxes (J m^{-2} s^{-1}) of energy caused by mass motions and f^Q is an internal/external energy supply (J m^{-3} s^{-1}).

2.1.2. Constitutive and equilibrium restrictions

A set of constitutive and equilibrium laws are required to express the various parameters or dependent variables of the mass balance equation (ω, ρ, S, E, $\mathbf{j}$, $\mathbf{i}_c$, etc.) as function of the state variables or independent variables (P_l, P_g and T). Examples are Darcy's law that relates liquid and gas advective fluxes to pressure gradients, Fourier's law that relates conductive heat flux to temperature gradient, retention curve that relates saturation to capillary pressure (P_g–P_l) and the psychometric law that relates vapour mass fraction to temperature and capillary pressure. A full list of all constitutive and equilibrium restrictions is given in chapter 3.

2.1.3. Standard boundary conditions

Boundary conditions and expressions for the source/sink terms (f^w, f^a and f^Q in (1), (2) and (3), respectively) have to be written for mass the mass balance equation for water, air and heat. RCB expresses nodal flow rates for every component (water, air and heat) and every phase (liquid, gas) as function of the state variables (P_l, P_g and T) and some prescribed values, specified by the user. For instance, the mass flow rate of water as a component of the gas phase (i.e., vapour) is:

$$j_g^w=\left(\omega_g^w\right)^0\left(j_g^0+\Delta j_g^0\frac{dt}{\Delta t}\right)+\left(\omega_g^w\right)^0\gamma_g\left(\left(P_g^0+\Delta P_g^0\frac{dt}{\Delta t}\right)-P_g\right)+\beta_g\left(\left(\rho_g\omega_g^w\right)^0-\left(\rho_g\omega_g^w\right)\right) \tag{4}$$

where the superscript $()^o$ stands for the prescribed values and the terms $\Delta(.)\ dt/\Delta t$ allow for imposing a linear variation of the variable (.) during the time step. This general form of boundary condition, includes three terms. The first one is the mass inflow or outflow that takes place when a flow rate of gas (j_g^0) is prescribed. Second term is the mass inflow or outflow that takes place when gas phase pressure (P_g^0) is prescribed at a node. The coefficient γ_g is a leakage coefficient, i.e., a parameter that allows a boundary condition of the Cauchy type. The third term is the mass inflow or outflow that takes place when vapour mass fraction is prescribed at the boundary. This term naturally comes from the nonadvective flux (Fick's law). Mass fraction and density prescribed values are only required when inflow takes place. For outflow the values in the medium are considered. The fluxes of different phase of a component are summed to obtain the total boundary condition of a component. For instance the mass flow of water is that in liquid and in gas:

$$j^w=j_l^w+j_g^w \tag{5}$$

For the energy balance equation, the boundary condition has a similar form.

$$j_e = \left(j_e^0 + \Delta j_e^0 \frac{dt}{\Delta t} \right) + \gamma_e \left(T^0 + \Delta T^0 \frac{dt}{\Delta t} - T \right) + E_g^w (j_g^w) + E_l^w (j_l^w) + E_g^a (j_g^a) + E_l^a (j_l^a) \qquad (6)$$

2.1.4. Atmospheric boundary conditions

RCB permits the simulation of meteorological/atmospheric phenomena, such as rain, evaporation, radiation and heat exchange between soil/atmosphere. These phenomena are simulated as flow boundary conditions for the three components (water, air and heat) written as functions of the state variables (P_l, P_g and T) or dependent variables (S_l, ω_g^w) and meteorological data that vary in time (atmospheric temperature and pressure, relative humidity, cloud index, rain fall and wind velocity). In what follows, these functions will be explained. Note, that positive fluxes are always considered into the modelled domain and negative fluxes outward. For instance, evaporation normally is negative, because it is a flux outward the domain.

The flux of water (j^w) is the sum of rainfall (P), evaporation (E), advective flux of vapour by the gas phase (j_g^w) and of surface runoff (j_{sr}):

$$j_w = P + E + j_g^w + j_{sr} \qquad (7)$$

Evaporation is given by an aerodynamic diffusion relation:

$$E = \frac{k^2 v_a \phi}{\left(\ln \frac{z_a}{z_0} \right)^2} \left(\rho_{va} - \rho_v \right) \qquad (8)$$

where ρ_{va} and ρ_v are the absolute humidity (mass of vapour per volume of gas, which can be calculate from relative humidity, H_r, and temperature) of the atmosphere and at the node of the boundary condition, respectively, k is the von Karman's constant (= 0.4), ϕ is the stability factor, z_0 is the roughness length, v_a is the wind velocity and z_a is the screen height at which v_a and ρ_{va} are measured. In theory, ρ_v must be the value at roughness length (z_0). Instead, RCB calculates ρ_v from the state variables at the node of the boundary condition. Hence, the same values are assumed at this node and at z_0.

The advective flux of vapour by the gas phase (j_g^w) is given by:

$$\begin{cases} j_g^w = \omega_g^w q_g & P_g > P_{ga} \\ j_g^w = \dfrac{\rho_{va}}{\rho_{ga}} q_g & P_g \le P_{ga} \end{cases} \qquad (9)$$

where P_{ga} is the atmospheric pressure, ρ_{ga} is the atmospheric gas density and q_g is the flux of the gas phase:

$$q_g = \gamma_g \left(P_g - P_{ga} \right) \tag{10}$$

where γ_g is a leakage coefficient. Surface runoff (j_{sr}) is written as:

$$\begin{cases} J_{sr} = \gamma_w \left(p_l - p_{ga} \right) & P_l > P_{ga} \\ J_{sr} = 0 & P_l \le P_{ga} \end{cases} \tag{11}$$

where γ_w is another leakage coefficient. It must be said that ponding is not explicitly simulated, that is, RCB does not have a special element representing storage of water in a pond. When one assumes no ponding a very high value for γ_w can be used (but no to high to avoid numerical instabilities). Then, if the soil is saturated ($P_l > P_{ga}$) all rainfall that cannot infiltrate will runoff.

For the flux of air only the advective part is considered:

$$J_a = \omega_g^a q_g = \left(1 - \omega_g^w \right) q_g \tag{12}$$

The energy flux (j_e) is divided into the sensible heat flux (H_s), convective or latent heat flux (H_c) and radiation (R_n):

$$J_e = H_s + H_c + R_n \tag{13}$$

The sensible heat flux (H_s) is, like evaporation, calculated through an aerodynamic diffusion relation:

$$H_s = \rho_{ga} C_a \frac{k^2 v_a \phi}{\left(\ln \frac{z_a}{z_0} \right)^2} \left(T_a - T_0 \right) \tag{14}$$

where C_a is the specific heat of the gas. The convective or latent heat flux (H_c) is calculated taking into account the internal energy of liquid water, vapour and air:

$$H_c = h_v \left(E + J_{wg} \right) + h_{la} \left(P + J_{wl} \right) + h_{a0} J_a \tag{15}$$

where h_v, h_{la} and h_{a0} are the free energy of vapour, liquid water and air, respectively. These three properties depend on the temperature, for which the temperature of the node of the boundary is taken for h_v, and h_{a0} and the dew point, which depends on the atmospheric vapour pressure, for h_{la}.

The radiation (R_n) can be given as a measured data or it can be calculated as:

$$R_n = \left(1 - A_l \right) R_g + \varepsilon R_a - \varepsilon \sigma T^4 \tag{16}$$

where R_g is the direct solar short wave radiation, R_a is the long wave atmospheric radiation, A_l is the albedo, ε is the emissivity, σ is the Stefan-Boltzman constant (5.67×10^{-8} J s^{-1} m^{-2} K^{-4}). Both the albedo and emissivity are considered function of the liquid saturation (S_l):

$$A_l = A_d + \left(A_d - A_w\right)\left(S_l^2 - 2S_l\right) \tag{17}$$

$$\varepsilon = 0.9 + 0.05 S_l \tag{18}$$

where A_d and A_w are the dry and wet albedo. The long wave atmospheric radiation (R_a) depends on the atmospheric temperature and absolute humidity according to an empirical relation:

$$R_a = \sigma T_a^{\,4}\left(0.605 + 0.048\sqrt{1370\rho_{va}}\right) \tag{19}$$

The calculation of the solar radiation (R_g) takes into account the time of the day and the year according to:

$$\begin{cases} R_g = \dfrac{\pi R_G}{2d_s}\sin\left(\dfrac{\left(t - t_m + 0.5d_s\right)\pi}{d_s}\right) & t_m - 0.5d_s \le t \le t_m + 0.5d_s \\ R_g = 0 & \text{otherwise} \end{cases} \tag{20}$$

where d_s is the time span between sunrise and sunset and t_m is the time at noon and R_G is the daily solar radiation calculated by an empirical relation:

$$R_G = \int_{t_m - 0.5d_s}^{t_m + 0.5d_s} R_g\,dt = R_A\left(0.29\cos\lambda + 0.52 I_n\right) \tag{21}$$

where λ is the latitude and I_n is the cloud index (= 1 for a clear sky, = 0 for a completely clouded sky) and R_A is the daily solar radiation in absence of atmosphere:

$$R_A = S_0 r_s\left[\frac{d_d}{\pi}\cos\lambda\cos\delta\sin\left(\frac{\pi d_s}{d_d}\right) + d_s\sin\lambda\sin\delta\right] \tag{22}$$

where S_0 is the sun constant (= 1376 J m^{-2} s^{-1}), r_s is the relation between the average distance between the earth and the sun and that of a given moment, d_d is the duration of a day (= 86400 s) and δ is the declination of the sun. The values of d_s, r_s and δ are calculated as follows:

$$d_s = \frac{d_d}{\pi}\operatorname{acos}\left(-\tan\lambda\tan\delta\right) \tag{23}$$

$$r_s = 1.00011 + 0.03422\cos\left(2\pi\frac{t - t_0}{d_a}\right) + 0.00128\sin\left(2\pi\frac{t - t_0}{d_a}\right) +$$

$$+0.000179\cos\left(4\pi\frac{t-t_0}{d_a}\right)+0.000077\sin\left(2\pi\frac{t-t_0}{d_a}\right) \quad (24)$$

$$\delta = -\delta_{\max}\sin\left(2\pi\frac{t-t_s}{d_a}\right) \quad (25)$$

where d_a is the duration of a year (= 365.241 days = 3.15568×10^7 s), t_0 is the time of January first, t_s is the time when autumn starts (September 21th at the northern hemisphere) and $\delta_{\max}$ is the maximum declination of the sun (= 0.4119 rad = 23.26°).

2.2. Chemical reactions

2.2.1. Species, reactions and stoichiometric coefficients

A chemical system is made up of a set of atomic constituents or elements. A chemical species is defined as any chemical entity distinguishable from the rest due to (1) its elemental composition, and (2) by the phase at which it is present. For instance, CO_2 gas is a different species than dissolved CO_2.

Components of a system are chemical entitites independent from each other that allow a complete description of the system. The selection of components is arbitrary, and depends on the system studied. Although the N_E atomic constituents or chemical elements could serve as a set of components, they are never used as such because the atomic constituents themselves are rarely present in aqueous phases. For this reason, it is more convenient to select as components a set of N_C aqueous species. These species are also known as the primary species.

From a mathematical point of view, defining a set of components amounts to finding a base in a vector space of chemical species. The set of N_E atomic constituents constitute the most intuitive base of the system, however, the set of N_C primary species represents a more practical one because the reactions among species can be quantitatively established. Since all bases must have the same size, it follows that $N_E = N_C$.

In a system made up of N_S chemical species, any of the N_R reactions taking place can be represented as a linear combination such as

$$\sum_{j=1}^{N_S}\nu_{ij}Q_j = 0 \qquad i = 1,\cdots N_R \quad (26)$$

where Q_j is the chemical formula of the j-th especies, and ν_{ij} is its stoichiometric coefficient in reaction i. The matrix $\mathbf{S}$ of stoichiometric coefficients is a N_R×N_S rectangular matrix having a range equal to N_R. If the reactions are independent, matrix $\mathbf{S}$

contains a non-singular square $N_R \times N_R$ submatrix. This means that it is possible (by forming appropriate linear combinations) to write matrix **S** in such a way that:

$$\mathbf{S} = \left(\mathbf{S_1} \middle| \mathbf{S_2}\right) \tag{27}$$

where $\mathbf{S_2}$ is a square matrix of size N_R and $\mathbf{S_1}$ is a rectangular $N_R \times (N_S - N_R)$ submatrix. This equation reflects that the chemical reactions in (26) can be rewritten so that a subset of N_R species (those corresponding to the columns of matrix $\mathbf{S_2}$) can be expressed as linear combinations of the remaining $(N_S - N_R)$ species. The N_R secondary species are related to the $(N_S - N_R)$ primary species. The entries of matrix **S** are:

$$\mathbf{S} = \begin{pmatrix} \nu_{11} & \nu_{12} & .. & \nu_{1N_c} & -1 & 0 & ... & 0 \\ \nu_{21} & \nu_{22} & .. & \nu_{2N_c} & 0 & -1 & ... & 0 \\ . & . & .. & . & . & . & ... & . \\ \nu_{N_R1} & \nu_{N_R2} & .. & \nu_{N_RN_C} & 0 & 0 & ... & -1 \end{pmatrix} \tag{28}$$

In RCB the entries ν_{ij} of matrix **S** are readed from one of the possible databases. Each database has a set of aquesous species considered primary. The rest of chemical species, called secondary species (aqueous complexes, minerals, gases, surface complexes) are expressed as lineal combinations of primary species. As a convention the stoichiometric coefficients are positive for species on the right hand side of the reaction, and negative for those on the left hand side. The reactions are written as dissociation reactions of one mole of secondary species, so that the resulting matrix $\mathbf{S_2}$ is **-I**. Once this initial matrix **S** is built from the database, a switch to any other set of primary species selected by the user is done automatically, as described below.

The choice of primary species is arbitrary. Secondary species correspond to the -1 columns of matrix **S** in (28). Should other species be selected as primary, the corresponding stoichiometric coefficients should be different. To illustrate the procedure to follow for defining a new set of primary species, let us consider the case where the second and fourth primary species in matrix **S** of (28) are specified as secondary. Their place is taken by the first and second previous secondary species. Imposing that the columns of secondary species are unit columns, one gets a new matrix **S'**:

$$\mathbf{S}' = \begin{pmatrix} \nu'_{11} & -1 & \nu'_{13} & 0 & .. & \nu'_{1N_c} & \nu'_{1N_C+1} & \nu'_{1N_C+2} & .. & 0 \\ \nu'_{21} & 0 & \nu'_{23} & -1 & .. & \nu'_{2N_c} & \nu'_{2N_C+1} & \nu'_{2N_C+2} & .. & 0 \\ . & . & . & . & .. & . & . & . & .. & . \\ \nu'_{N_R1} & 0 & \nu'_{N_R3} & 0 & .. & \nu'_{N_RN_c} & \nu'_{N_RN_C+1} & \nu'_{N_RN_C+2} & .. & -1 \end{pmatrix} \tag{29}$$

Whose entries are different from those of **S**, but can be obtained in a similar manner. The two matrices **S** and **S'** are related through a linear matrix operator $\boldsymbol{\beta}(N_R \times N_R)$:

$$\mathbf{S}' = \boldsymbol{\beta}\mathbf{S} \tag{30}$$

The entries of $\boldsymbol{\beta}$ can be obtained taking into account that $\boldsymbol{\beta}$ is able to give the identity submatrix $-\mathbf{I}$ of size $N_C \times N_C$ of matrix $\mathbf{S}'$ (formed by the second, fourth and last columns in the previous example) from the equivalent submatrix $\mathbf{S_2}$ (formed by the same columns) of $\mathbf{S}$:

$$-\mathbf{I} = \boldsymbol{\beta}\mathbf{S_2} \tag{31}$$

and therefore

$$\boldsymbol{\beta} = -\mathbf{S_1}^{-1} \tag{32}$$

In general, $\mathbf{S_2}$ is a square matrix of size $N_R \times N_R$ containing the N_R columns of $\mathbf{S}$ corresponding to the new set of secondary species.

2.2.2. Chemical equilibrium

When local equilibrium is assumed among chemical species of the system, at a given pressure and temperature, the Gibbs free energy of the system reaches a minimum, and the system cannot spontaneously carry out any chemical work. The derivation from this principle of equilibrium (Denbigh, 1987) leads to the well known mass action law expression:

$$a_j^{-1} \prod_{i=1}^{N_C} a_i^{\nu_{ji}} = K_{j(p,T)} \tag{33}$$

where K_j is the equilibrium constant which depends on the pressure and temperature of the system. a_i and a_j are the thermodynamic activity of the ith and jth species, respectively; N_C is the total number of primary species and ν_{ji} is the stoichiometric coefficient of the ith primary species in the dissociation reaction of the jth species. RCB allows the equilibrium constants to depend on the temperature according to:

$$\ln K = f_1 \ln T + f_2 + f_3 T + f_4 / T + f_5 / T^2 \tag{34}$$

where f_1 to f_5 are coefficients obtained by fitting.

Eq (33) shows that K_j depends on the stoichiometric coefficients ν_{ji} of the species involved in the j-th reaction. Therefore, if the set of primary species is modified, the equilibrium constant will change accordingly. From (33) it follows that:

$$\ln K_j = \ln a_j + \sum_{i=1}^{N_C} \nu_{ji} \ln a_i \tag{35}$$

which in matrix form becomes:

$$\ln \mathbf{k} = -\mathbf{S} \ln \mathbf{a} \tag{36}$$

where $\mathbf{k}$ is the column vector of K_j values, $\mathbf{S}$ is the matrix of stoichiometric coefficients (see Eq. (28)), and $\mathbf{a}$ is the column vector the activity of the species. For a different set of primary species having a $\mathbf{S'}$ coefficient matrix, the corresponding $\mathbf{k'}$ values will be given by:

$$\ln \mathbf{k}' = -\mathbf{S}' \ln \mathbf{a} \tag{37}$$

Notice that vector $\mathbf{a}$ remains the same as long as pressure and temperature remain constant. From (30), (36) and (37) one has:

$$\ln \mathbf{k'} = -\mathbf{S'} \ln \mathbf{a} = -\boldsymbol{\beta}\mathbf{S} \ln \mathbf{a} = \boldsymbol{\beta} \ln \mathbf{k} \tag{38}$$

which means that ln $\mathbf{k'}$ is computed from ln $\mathbf{k}$ through the linear $\boldsymbol{\beta}$ operator.

2.2.3. Aqueous complexation

Aqueous complexation reactions are those which take place in the aqueous phase including acid-base and redox reactions.

The continuous motion of dissolved ions together with their large number per unit volume cause numerous collisions making possible the formation of ion pairs and/or dissolved complexes which usually have an ephimerous live (on the order of 10^{-10} s). Since these reactions are almost instantaneous, they can be effectively considered as equilibrium reactions. The equilibrium constant relates the average number of ions pairs or complexes which are being formed. Applying the Mass-Action Law to the dissociation of the *j*-th secondary species, one has:

$$\ln \mathbf{k_a} = -\ln \mathbf{a_2} + \mathbf{S_a} \ln \mathbf{a_1} \tag{39}$$

where $\mathbf{a_1}$ and $\mathbf{a_2}$ are vector containing the thermodynamic activities of the primary and secondary aqueous species, respectively, and $\mathbf{S_a}$ is the matrix with stoichiometric coefficients. This equation allows one expressing the concentration of secondary species or aqueous complexes $\mathbf{c_{a2}}$ in terms of primary species concentrations $\mathbf{c_{a1}}$ (both in mol/kg water):

$$\mathbf{c_{a2}} = -\ln \mathbf{k_a} - \ln \boldsymbol{\gamma}_\mathbf{a2} + \mathbf{S_a} \ln \mathbf{c_{a1}} + \mathbf{S} \ln \boldsymbol{\gamma}_\mathbf{a2} \tag{40}$$

where $\boldsymbol{\gamma}_\mathbf{a1}$ and $\boldsymbol{\gamma}_\mathbf{a2}$ are vectors with thermodynamic activity coefficients of primary and secondary aqueous species, respectively.

For non-concentrated solutions (less than 1 mol/kg) the value of the activity coefficient of the *i*-th aqueous species can be calculated according to the extended Debye-Hückel formula:

$$\log \gamma_{ai} = -\frac{A z_i^2 (I)^{\frac{1}{2}}}{1 + B a_i (I)^{\frac{1}{2}}} + bI \tag{41}$$

where I is the ionic strength of the solution; z_i and a_i are the electric charge and the ionic radius in solution of the i-th aqueous species, respectively; A and B are constants which depend on temperature and dielectric constant of water, and b is a constant determined from fitting experimental data. The values of A, B and b at different temperatures are tabulated in Helgeson and Kirkham (1974). The value of the ionic strength is calculated as:

$$I = \frac{1}{2} \sum_{i=1}^{N_C} c_{ai} z_i^2 \tag{42}$$

Another way to calculate the activity coefficient is by means of the formula of Truesdell-Jones. This formula is the same as equation (41) except that b does not depend on the temperature but on the species, that is, every species has its own value for b.

The activity of water can be calculated according to the approximation of Garrels and Christ (1965):

$$a_{H_2O} = 1 - 0.018 \sum_{i=2}^{N_S} c_i \tag{43}$$

where N_S is the number of aqueous species.

The vector of total aqueous concentration of the components $\mathbf{u_a}$ can be written in an explicit form as a function of the concentration of the N_C primary species:

$$\mathbf{u_a} = \mathbf{c_{1a}} + \left(\mathbf{S_a}\right)^T \mathbf{c_{2a}} = \mathbf{c_{1a}} + \left(\mathbf{S_a}\right)^T \exp\left(-\ln \mathbf{k_a} - \ln \boldsymbol{\gamma}_{\mathbf{a2}} + \mathbf{S_a} \ln \mathbf{c_{a1}} + \mathbf{S} \ln \boldsymbol{\gamma}_{\mathbf{a2}}\right) \tag{44}$$

As shown before, the chemical composition of an aqueous system containing N_S species can be expressed in terms of the concentrations of N_C components (primary species). This is of great relevance for reactive solute transport modeling because instead of N_S transport equations only N_C equations have to be solved. The concentration of the (N_S − N_E) aqueous secondary species can be explicitly computed from the concentrations of primary species. This results in a significant reduction of computing time.

The transfer of electrons between two different atoms changes their chemical valence. This transfer is known as an oxidation-reduction reaction. The redox potential of a chemical system can be described by means of redox pairs such as O_2/H_2O, SO_4^{2-}/H_2S, Fe^{3+}/Fe^{2+}, CO_2/CH_4, etc... Usually, the redox potential is governed by the most abundant redox pair. Even though this approach seems to be the most adequate, it is rarely used due to the difficulty of obtaining the analytical concentrations of the two species of a redox pair.

Among the different alternative approaches to describe redox reactions the external approach considers hypothetical electron activity as an aqueous component or a primary species. Contrary to the protons, which exist in reality as dissolved species, the electron concentration is a hypothetical variable. The definition of this virtual concentration is useful because it allows to complete the redox half-reactions and treat them as the rest

of the chemical reactions in the aqueous phase. Each half redox reaction is completed by adding electrons as transferable species. The activity coefficient of this hypothetical species is assumed to be equal to one. It is possible then to define the total electron concentration C_e as:

$$u_{ae} = \sum_{j=1}^{N_S - N_C} S_{a,je} c_{2a,j} \tag{45}$$

where $S_{a,je}$ is the stoichiometric coefficient of the electron in j-th half-redox reaction. Unlike equation (44), $c_{a1,e}$ (the virtual "free electron concentration") does not participate in the calculation of the total, because it does not actually exist.

Similar to acid-base reactions, the total concentration $u_{a,e}$ represents the net electron balance or "electron excess" for all redox reactions. Thus, $u_{a,e}$ may take on positive or negative values. In this way, redox reactions can be treated in the same way as the rest of equations.

Once the “free electron concentration”, $c_{a1,e}$, is known, the calculation of other redox indicators, such as the counter-part species of a redox pair, the concentration of disolved oxygen ($O_{2(aq)}$), or the fugacity of oxygen gas ($O_{2(g)}$), can be easily calculated by considering them as secondary species according to Eqn. (40).

2.2.4. Adsorption reactions

Adsorption of aqueous species on the surface of solids has been described according to several empirical relationships and thermodynamic models. The empirical relationships are experimental partition coefficients between the solute in solution and the solute adsorbed. The relationships included in the RCB code are the K_D, Freundlich, and Langmuir equations, and the ion exchange model. The thermodynamic models are based on surface complexation reactions, and are similar to the aqueous complexation reactions described above, although an electrostatic term accounts for the electric field created by the charged species sorbed on the solid surfaces. Similarly to aqueous reactions, surface complexation reactions are fast reactions, and the RCB code assumes that chemical equilibrium is reached. From complex to simple, the thermodynamic models included in RCB are: the triple layer, diffuse layer, the constant capacitance and the non-electrostatic models. We will describe the different adsorption models, starting with the most complex thermodynamic models, following by the empirical relationships.

2.2.4.1. Electrostatic models

Many minerals such as metal oxides, hydroxides and layered silicates (Al_2O_3, TiO_2, FeOOH, SiO_2, kaolinite, etc.) exhibit electrically charged surfaces in the presence of natural waters. These surfaces contain ionizable functional groups (ex.: silanol groups in hydrated silica: Si-OH), being responsible for chemical reactions at the surface.

The sorption of solute at the solid surfaces are described as chemical reactions between the aqueous species and specific surface sites (surface complexation). These surface reactions include proton exchange, cation binding and anion binding via ligand

exchange at surface hydroxil sites (represented here as XOH to avoid confusion with other chemical species). For example, the desorption of a metal could be represented as:

$$\mathrm{XOM}^{z+-1} + \mathrm{H}^{+} \rightleftharpoons \mathrm{XOH} + \mathrm{M}^{z+} \tag{46}$$

At equilibrium the sorption reactions can be described by the mass law equation

$$K_{\text{int}} = \frac{\left[\mathrm{XOH}\right] a_{\mathrm{M}^{z+}}}{\left[\mathrm{XOM}^{z+-1}\right] a_{\mathrm{H}^{+}}} \tag{47}$$

where K_{int} is the equilibrium constant related to the chemical reaction, usually refered to as the intrinsic constant (Dzombak and Morel, 1990), a is the thermodynamic activity of the aqueous species (the product of the concentration in mol/kg water per a coefficient γ), and the terms in brackets represent the concentration of surface complexes (mol/kg water). As a first approach the ideal behaviour of surface complexes is assumed in the previous formulation, i.e., a particular surface complex is not influence by the rest of sites (empty or full) in the neighbourhood. We will discuss later the non ideal behaviour as a surface electric potential.

In aqueous complexation reactions the electric charge is assumed to be homogeneously distributed in the solution. However, surface reactions take place on a fixed charged surface which creates an electrostatic field. An additional energetic term accounting for the work needed for the aqueous species to travel across the surface electric field is required:

$$\Delta G_{ads} = \Delta G_{\text{int}} + \Delta G_{coul} = \Delta G_{\text{int}} + \left(\Delta G_{\psi=0} - \Delta G_{\psi=\psi_0}\right) = \Delta G_{\text{int}} + \Delta z F \psi_0 \tag{48}$$

where ΔG is the free enthalpy change of the overall adsrption reaction, ΔG_{int} and ΔG_{coul} are the free enthalpy change due to chemical bonding and to the electrostatic work, respectively, Δz is the change in the charge of the surface species, F the Faraday's constant (96485 C/mol) and ψ_0 is the mean surface potential (V). Since:

$$\Delta G = -RT \ln K \tag{49}$$

Equation (47) can be rewritten as:

$$K_{ads} = K_{\text{int}} \exp\left(\frac{-\Delta z F \psi_0}{RT}\right) \tag{50}$$

where R is the gas constant (8.314 J/mol/K) and T the absolute temperature (K), K_{ads} the apparent equilibrium constant of the overall adsorption process and K_{int} does not depend on the surface charge. Although the contribution of the electrostatic term to the total sorption energy is not determined experimentally, it is useful to take into account the variations of surface charge effects on surface complexation reactions. In Eqns. (47) and (50) the thermodynamic activities of the surface complexes are substituted by their concentrations. This is based on the assumption that all non ideal behaviour of the

surface species is attributed to the mean surface potential and is accounted for by the electrostatic term.

By considering the electrostatic term in the equilibrium formulation a new unknown, the mean surface potential, ψ_0 is introduced. A new equation to find the solution of the problem is, therefore, required.

Several theoretical models describe the value of capacitance of the surface, i.e., the relationship between the mean surface potential and the charge density. In increasing order of complexity, these models are: the constant capacitance model, the diffuse layer model and the triple layer model. The option for a particular model depends on the amount of experimental data needed to obtain the equilibrium constant of the reactions. We will discuss first the triple layer model because it includes the other two as particular cases.

The triple layer model

The triple layer model was developed by Davies and Leckie (1978) to be applied to adsorption of metals on oxide surfaces. All sorbed ions are ascribed to one of two surface layers, 0 and β, whereas a diffuse layer, d, is formed with counter ions in solution. Some surface reactions, such as protonation and de-protonation, take place at the immediate surface of the mineral or 0 layer. This layer has a total surface charge σ_0 and a potential ψ_0. Other ions in solution are bounded to protonated/de-protonated groups of opposite sign and create a layer β with a charge σ_β and a potential ψ_β. The surface charge of layers 0 and β is calculate from the total surface species adsorbed on the layer:

$$\sigma_0 = \frac{F}{A}\sum_{k=1}^{N_0} z_k y_k \tag{51}$$

$$\sigma_\beta = \frac{F}{A}\sum_{k=1}^{N_\beta} z_k y_k \tag{52}$$

where F is the Faraday constant (C/mol), A is the specific surface area (m^2/kg water), z_k and y_k are the charge and the concentration of the k-th adsorbed species (mol/kg water), respectively; and N_0 and N_β are the number of species adsorbed in layers 0 and β, respectively (N_0 + N_β = N_y). The value of A is currently found in literature as the product $S\times A$, where S is the solid concentration (g/kg water), and A is the surface area of the solid per unit of mass (m^2/g).

A number of solvated ions in solution do not neutralize the surface charge by forming surface complexes, but by means of a zone of major density of delocalized ions of sign opposite to that of the surface. The surface charge and the potential of this diffuse layer of counterions are related by Guy-Chapman or double-layer theory:

$$\sigma_d = \sqrt{8RT\varepsilon\varepsilon_0 I}\,\sinh\left(F\psi_d / RT\right) \tag{53}$$

where ε is the dielectric constant of water, ε_0 the permitivity of free space (8.854x10^{-12} C/V/m), and I the ionic strength of the solution (mol/kg water).

The 0 and β layers are separated by a region of capacitance C_1, and the layers β and d are separated by a region of capacitance C_2. The surface charge of the three layers is also related to potentials by electrostatic capacitances, and also verify that the total surface charge is zero ($\sigma_0 + \sigma_\beta + \sigma_d = 0$):

$$\sigma_0 = C_1\left(\psi_0 - \psi_\beta\right) \tag{54}$$

$$\sigma_\beta = C_1\left(\psi_\beta - \psi_0\right) + C_2\left(\psi_\beta - \psi_d\right) \tag{55}$$

$$\sigma_d = C_2\left(\psi_d - \psi_\beta\right) \tag{56}$$

The values of C_1 and C_2 (F/m^2) are normally obtained by fitting experimental data.

The diffuse layer model

The diffuse layer model has been fully described by Dzombak and Morel (1990) and applied to adsorption of metals on iron oxide surfaces. In the diffuse layer model the solid-water interface is composed by two layers: a layer of surface-bounded complexes and a diffuse layer of counter ions in solution. All the sorbed ions are assigned to the unique surface layer, whose surface charge is calculated according to an equation similar to Eqn. (51) or Eqn. (52). Similar to the triple-layer model the relationship between the surface charge and the potential can be calculated from the Guy-Chapman theory Eqn. (53).

One normally uses a linearized expression for low values of the potential:

$$\sigma_d = \varepsilon\varepsilon_0\kappa\psi \tag{57}$$

where $1/\kappa$ (m) is the double-layer thickness:

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon\varepsilon_0 RT}{20F^2 I}} \tag{58}$$

Therefore, in the diffuse-layer model the value of the capacitance C relating the surface charge and the potential can be calculated based on theoretical considerations, Eqn. (57), instead of being an experimental fitting parameter.

The constant capacitance model

The constant capacity model has been introduced among others by Schindler et al. (1976). As in the diffused-layer the constant capacitance model is based on the assumption that all the species are sorbed in the same layer and a diffuse layer of counterions constitutes the transition to homogenous solution. However, differently

from the diffuse-layer model the relationship between the surface charge and the potential is assumed here to be linear and constant:

$$\sigma = C\psi \tag{59}$$

where C is a constant value to be obtained from fitting experimental data.

Non-electrostatic thermodynamic model

Owing to the difficulties of obtaining the capacitance parameters from experimental data, most of experiments are currently modelled assuming ideal behaviour of the sorbed species, i.e. no electrostatic field exists at the adsorbing surface (ΔG_{coul} = 0 in Eq. (48)). Therefore, this model is a simple equilibrium model as described by Eq. (47).

Mathematical formulation of electrostatic adsorption

A more general mathematical description of thermodynamic adsorption modelling can be formulated. To do so, lets assume the surface desorption reaction of Eqn. (46) with the equilibrium constant of Eqn. (50). In order to represent the adsorbed species an additional set of N_X components has to be added to the initial set of N_C aqueous primary species. The new species are:

- Triple layer model: $N_X = 4$, $c_{x,1} = c_{\mathrm{XOH}}$, $c_{x,2} = \exp(-F\psi_0/RT)$, $c_{x,3} = \exp(-F\psi_\beta/RT)$, $c_{x,4} = \exp(-F\psi_d/RT)$.
- Diffuse Layer model and Constant Capacitance model: $N_X = 2$, $c_{x,1} = c_{\mathrm{XOH}}$, $c_{x,2} = \exp(-F\psi_0/RT)$.
- Non-electrostatic model: $N_X = 1$, $c_{x,1} = c_{\mathrm{XOH}}$.

The vector of concentrations of a surface complex, $\mathbf{c_d}$, (mol/kg water) can be expressed in terms of the concentration of the two sets of components:

$$\ln \mathbf{c_d} = -\ln \mathbf{k_d} + \mathbf{S_d} \ln \mathbf{c_{a1}} + \mathbf{S_d} \ln \boldsymbol{\gamma}_{\mathbf{a1}} + \mathbf{S_x} \ln \mathbf{c_x} \tag{60}$$

where $\mathbf{k_d}$ is the equilibrium constant of the desorption reaction, and $\mathbf{S_x}$ is the stoichiometric matrix of the additional components, which values are:

- Triple Layer model: $S_{x,j1} = S_{x,\mathrm{XOH}}$; $S_{x,j2} = z_j^0$; $S_{x,j3} = z_j^\beta$; $S_{x,j4} = 0$
- Diffuse Layer model and Constant Capacitance model: $S_{x,j1} = S_{x,,\mathrm{XOH}}$; $S_{x,j2} = z_j^0$
- Non-electrostatic model: $S_{x,j1} = S_{x,,\mathrm{XOH}}$

where z_j is the electrostatic charge of the surface complex.

The concentration of total sorption sites (mol/kg water) is calculated as follows:

$$T_X = c_{x,1} + \sum_{j=1}^{N_d} S_{x,j1} c_{d,j} \tag{61}$$

where $c_{x,1}$ is the concentration of the XOH additional component.

2.2.4.2. Empirical relationships

These models are descriptions of experimental relationships between the concentration of solute in solution and the concentration of solute sorbed on the solid surface. As the experiments are performed at constant temperature these models are also known as isotherms.

The K_D linear isotherm

Following the treatment of previous electrostatic models, the desorption reaction of a metal with no electrostatic terms is:

$$\mathrm{XM} \rightleftharpoons \mathrm{X} + \mathrm{M} \tag{62}$$

As in previous models the equilibrium constant for the desorption reaction will be:

$$K_{ads} = \frac{a_{\mathrm{X}} a_{\mathrm{M}}}{a_{\mathrm{XM}}} \tag{63}$$

The K_D model is based on the following assumptions

- the concentration of surface sorbing sites is very high, and it is not affected by the amount occupied by sorbed metals ($a_{\mathrm{X}} = 1$);
- the amount of surface sites occupied by metals is very small and has no influence on the behaviour of the neibourgh sites, i.e., the sorbed metals behave ideally and the standard state is a solid with 1 mol/kg sites occupied by the metal ($a_{XM}=c_{XM}$, in mol/kg);
- there is no aqueous speciation in the solution, i.e., the total solute is represented by one aqueous species ($u_{\mathrm{M}} = c_{\mathrm{M}}$);
- the solute behaves ideally in solution ($\gamma_{\mathrm{M}} = 1$).

Taking into account these assumptions the equilibrium constant of the desorption reactions results:

$$K_{ads} = \frac{u_{\mathrm{M}}}{c_{\mathrm{XM}}} \tag{64}$$

where c_{XM} is the concentration of sorbed solute (mol/kg), u_{M} is the total concentration of solute in the solution (mol/kg). Eqn. (64) is identical to the common expression of the K_D model, saying that the amount of solute sorbed on the surface is proportional to the amount of solute in solution:

$$c_{\mathrm{XM}} = K_d u_{\mathrm{M}} \tag{65}$$

where in our case:

$$K_{ads} = \frac{1}{K_D} \tag{66}$$

The non-linear Freundlich isotherm

This model is based on the same assumptions than the K_D model, and can be treated in identical way. The only difference is that in the Freundlich model the amount of sorbed metal is proportional to the concentration of metal in solution elevated to a power exponent, η, determined experimentally:

$$c_{\mathrm{XM}} = K_L u_{\mathrm{M}}^{\eta} \tag{67}$$

In the case of $\eta = 1$ the Freundlich model is identical to the K_D model.

The Langmuir model

The Langmuir model is based on the following assumptions:
- the concentration of surface sorbing sites is not very high but limited. Therefore, there is a competition of the different aqueous species for the surface sorption sites, which must be considered in the calculations;
- the free sorbing sites are not influenced by the near by sites, i.e., they behave ideally, and the standard state is a solid with 1 mol/kg of free sites ($a_{\mathrm{X}} = c_{\mathrm{X}}$ in mol/kg).

As the K_D and Freundlich models:
- the amount of surface sites occupied by metals has no influence on the behaviour of the near by sites, i.e., the sorbed metals behave ideally and the standard state is a solid with 1 mol/kg sites occupied by the metal ($a_{\mathrm{XM}} = c_{\mathrm{XM}}$ in mol/kg);
- there is no aqueous speciation in the solution, i.e., the total solute is represented by one aqueous species ($u_{\mathrm{M}} = c_{\mathrm{M}}$);
- the solute behaves ideally in solution ($\gamma_{\mathrm{M}} = 1$).

Therefore, Eqn. (63) will be in the present case:

$$K_{ads} = \frac{c_{\mathrm{X}} u_{\mathrm{M}}}{c_{\mathrm{XM}}} \tag{68}$$

where the constant of the desorption reaction is:

$$K_{ads} = \frac{1}{K_L} \tag{69}$$

being K_L the adsorption coefficient experimentally determined.

There is an equivalence of Eqn. (68) with the known expression of the Langmuir isotherm. Let's consider the simple case of desorption of a cation M. The total surface sorption sites T_{X} (mol/kg) is:

$$T_{\mathrm{X}} = c_{\mathrm{X}} + c_{\mathrm{XM}} \tag{70}$$

replacing c_{X} in Eqn. (70) for its value from Eqn. (68) and K_{ads} for its value in Eqn. (69), the following expression is obtained:

$$c_{\mathrm{XM}} = T_{\mathrm{X}} \frac{K_L u_{\mathrm{M}}}{1+K_L u_{\mathrm{M}}} \tag{71}$$

changing the units of concentration c_{X} (mol/Kg water) to Γ mol/g solid, and consider the concentration of total sorption sites T_{X} as the maximum sorption capacity $\Gamma_{\max}$ (mol/g solid), the well-known expression of the Langmuir isotherm is obtained:

$$\Gamma = \Gamma_{\max} \frac{K_L u_{\mathrm{M}}}{1+K_L u_{\mathrm{M}}} \tag{72}$$

Mathematical formulation of non-electrostatic models

The calculation of the non-electrostatic models is similar to that explained for the electrostatic ones, the concentration of a sorbed species, y_j, (mol/kg water) can be expressed in terms of the concentration of the two sets of components, c and s (Eqn. 2.2.35). The value of N_S, s_k and   is as follows:

- K_D and Freundlich models: $N_X = 1$, $c_{x,1} = 1$, $\gamma_i = 1$, $S_{x,j1} = 1$
- Langmuir model: $N_X = 1$, $c_{x,1} = c_{\mathrm{X}}$, $\gamma_i = 1$, $S_{x,j1} = 1$

2.2.4.3. Cation exchange

Cation exchange takes place when an exchangeable cation located on the surface and interlayers of minerals is exchanged with a cation in the solution. The main difference with the surface complexation models and the empirical relationships previously described lays in the fact that no free sorption sites are assumed, and the capture of a cation from the solution is always coupled with the release of a cation from the surface.

Therefore, for monocharged cations the exchange can be described as a reaction:

$$\mathrm{I}^+ + (\mathrm{X\text{-}J}) \rightleftharpoons (\mathrm{X\text{-}I}) + \mathrm{J}^+ \tag{73}$$

where (X-I) and (X-J) denote the exchangeable site occupied by the I and J ions, respectively. As any reaction, there is an equilibrium constant associated to it:

$$K_{\mathrm{I/J}} = \frac{a_{\mathrm{J}} a_{(\mathrm{X\text{-}I})}}{a_{\mathrm{I}} a_{(\mathrm{X\text{-}J})}} \tag{74}$$

where the activities of the ions in solution, a_{I} and a_{J} are calculated according to the Debye-Hückel theory. There is no consensus, however, to describe the non-ideal behavior of the ions attached to the exchangeable sites. Three main different conventions are still in use in current literature: Gaines-Thomas, Gapon and Vanselov conventions. The code CBR uses the Gaines-Thomas convention.

According to the Gaines-Thomas convention the general expression for cation exchange reactions is:

$$\frac{1}{z_{\mathrm{I}}}\mathrm{I}^{z_{\mathrm{I}}}+\frac{1}{z_{\mathrm{J}}}\left(\mathrm{X}_{z_{\mathrm{J}}}\text{-J}\right)\rightleftharpoons\frac{1}{z_{\mathrm{I}}}\left(\mathrm{X}_{z_{\mathrm{I}}}\text{-I}\right)+\frac{1}{z_{\mathrm{J}}}\mathrm{J}^{z_{\mathrm{J}}} \tag{75}$$

where z is the electric charge of the cation. The expression (X_z-I) indicates that each exchangeable cation occupies z exchangeable sites.

According to this convention the activity of an exchangeable cation is approximated to its equivalent fraction, i.e., the standard state (activity equal 1), is an exchanger solid with all the sites occupied by the cation of interest:

$$a\left(\mathrm{X}_{z_{\mathrm{I}}}\text{-I}\right)=\beta_{\mathrm{I}}=\frac{\left[\mathrm{X}_{z_{\mathrm{I}}}\text{-I}\right]_{eq}}{\sum_{\mathrm{J}=1}^{\mathrm{J}=N_Y}\left[\mathrm{X}_{z_{\mathrm{J}}}\text{-J}\right]_{eq}}=\frac{z_{\mathrm{I}}\left[\mathrm{X}_{z_{\mathrm{I}}}\text{-I}\right]_{\mathrm{M}}}{CEC} \tag{76}$$

where $[X_{zi}\text{-I}]_{eq}$ and $[X_{zi}\text{-I}]_{M}$ are the number of equivalents and moles of the exchangeable cation per kg of water respectively; β_I is the equivalent fraction, *CEC* is the cation exchange capacity (in equivalents per kg of water), and N_Y the total number of exchangeable cations.

Therefore, the approximate equilibrium constant or exchange coefficient for the reaction under the Gaines-Thomas convention is:

$$K_{\mathrm{I/J}}=\frac{a_{\mathrm{J}}^{\frac{1}{z_{\mathrm{J}}}}\beta_{\mathrm{I}}^{\frac{1}{z_{\mathrm{I}}}}}{a_{\mathrm{I}}^{\frac{1}{z_{\mathrm{I}}}}\beta_{\mathrm{J}}^{\frac{1}{z_{\mathrm{J}}}}} \tag{77}$$

Mathematical formulation of exchange reactions

It is possible to calculate the cation exchange reactions as surface complexation reactions by splitting the overall exchange reaction into two "half-reactions" of the two cations involved with a hypothetical exchange site X. The reasoning is similar to that of the redox reactions and the hypothetical "free electron". For example, the exchange reaction:

$$\mathrm{Na}^{+}+\frac{1}{2}\left(\mathrm{X}_2\text{-Ca}\right)\rightleftharpoons\left(\text{X-Na}\right)+\frac{1}{2}\mathrm{Ca}^{2+}\qquad K_{\mathrm{Na/Ca}} \tag{78}$$

can be described by combining the two following "half-reactions":

$$\text{X-Na}\rightleftharpoons\mathrm{X}^{-}+\mathrm{Na}^{+}\qquad K_{\text{X-Na}} \tag{79}$$

$$\mathrm{X}_2\text{-Ca}\rightleftharpoons 2\mathrm{X}^{-}+\mathrm{Ca}^{2+}\qquad K_{\text{X2-Ca}} \tag{80}$$

The first problem arises to calculate the value of the exchange coefficient for the "half-reactions", from the experimental value of the coupled exchange reactions. The mathematical treatment of this problem varies according to the starting convention used.

When assuming the Gaines-Thomas convention, let's consider two half-reactions with their equilibrium constants:

$$\left(\mathrm{X}_{z_\mathrm{I}}\text{-I}\right) \rightleftharpoons z_\mathrm{i}\mathrm{X}^- + \mathrm{I}^{z_\mathrm{I}} \qquad K_\mathrm{I} \tag{81}$$

$$\left(\mathrm{X}_{z_\mathrm{J}}\text{-J}\right) \rightleftharpoons z_\mathrm{J}\mathrm{X}^- + \mathrm{J}^{z_\mathrm{J}} \qquad K_\mathrm{J} \tag{82}$$

and the value of the exchange coefficient is:

$$K^*_{\mathrm{I/J}} = \left(K_\mathrm{I}\right)^{-\frac{1}{z_\mathrm{I}}} \left(K_\mathrm{J}\right)^{\frac{1}{z_\mathrm{J}}} \tag{83}$$

where $K^*_{\mathrm{I/J}}$ is a product of activities. According to the standard state defined for surface complexation reactions (see 2.2.4.1.), the activities of ions in solution is calculated according to the Debye-Hückel formula, and the activities of surface complexes, are initially equated to their molar concentration (mol/kg water), assuming ideal behaviour:

$$K^*_{\mathrm{I/J}} = \frac{a_\mathrm{J}^{\frac{1}{z_\mathrm{J}}} \left[\mathrm{X}_{z_\mathrm{I}}\text{-I}\right]_\mathrm{M}^{\frac{1}{z_\mathrm{I}}}}{a_\mathrm{I}^{\frac{1}{z_\mathrm{I}}} \left[\mathrm{X}_{z_\mathrm{J}}\text{-J}\right]_\mathrm{M}^{\frac{1}{z_\mathrm{J}}}} \tag{84}$$

Therefore, a conversion factor is required to transform the value of $K_{\mathrm{I/J}}$, experimentally determined, into the value of $K^*_{\mathrm{I/J}}$. Taking into account the value of β_I, Eqn. (76), the value of $K^*_{\mathrm{I/J}}$ can be expressed as:

$$K^*_{\mathrm{I/J}} = \frac{a_\mathrm{J}^{\frac{1}{z_\mathrm{J}}} \beta_\mathrm{I}^{\frac{1}{z_\mathrm{I}}}}{a_\mathrm{I}^{\frac{1}{z_\mathrm{I}}} \beta_\mathrm{J}^{\frac{1}{z_\mathrm{J}}}} \frac{CEC_\mathrm{I}^{\frac{1}{z_\mathrm{I}}} z_\mathrm{J}^{\frac{1}{z_\mathrm{J}}}}{CEC_\mathrm{J}^{\frac{1}{z_\mathrm{J}}} z_\mathrm{I}^{\frac{1}{z_\mathrm{I}}}} \tag{85}$$

where the first fraction is the value of $K_{\mathrm{I/J}}$, and the second fraction a conversion factor.

From Eqns. (83) and (85) the value of the exchange coefficient K_J for the desorption half-reaction can be expressed as:

$$K_\mathrm{J} = \left(K_\mathrm{I}\right)^{\frac{z_\mathrm{J}}{z_\mathrm{I}}} CEC^{\frac{z_\mathrm{J}}{z_\mathrm{I}}-1} z_\mathrm{J} z_\mathrm{I}^{\frac{z_\mathrm{J}}{z_\mathrm{I}}} \left(K_{\mathrm{I/J}}\right)^{z_\mathrm{I}} \tag{86}$$

where $K_{\mathrm{I/J}}$ is the experimental exchange coefficient of the coupled exchange reaction, CEC is the solid exchange capacity (in eq./kg water); z_i and z_j are the electric charges of the i-th and j-th cations, respectively; and K_I is the equilibrium constant of the desorption half-reaction of a reference cation (commonly Na^+), which must be fixed arbitrarily. In fixing the value of K_I one must take into account that no free sorption sites

are assumed in the cation exchange models. A value for K_I of 10^{-20} (Appelo, 1994) ensures insignificant concentrations for X, and numerical stability for most of exchangeable cations. All these calculations are made internally in the code CBR, whereas the database contains the exchange reactions as half-reactions, $K_I = K_{X\text{-}Na} = 1$, and $K_J = K_{I/J}$.

Once the half-reactions are stablished, the concentration of cations sorbed as exchanged cations, $\mathbf{c_d}$, can be calculated from the concentration of primary aqueous species and the concentration of "free sorption site", c_{x1} (in mol/kg water), which is always a very low value. The mathematical treatment explained for the case of non-electrostatic adsorption can easily be applied to exchange half-reactions. Thus, the concentration (mol/kg) of sorbed cation is calculated as:

$$\ln \mathbf{c_d} = -\ln \mathbf{k_d} + \mathbf{S_d} \ln \mathbf{c_{a1}} + \mathbf{S_d} \ln \boldsymbol{\gamma}_{\mathbf{a1}} + \mathbf{S_x} \ln \mathbf{c_x} \tag{87}$$

and the conservation of the mass of exchangeable sites:

$$T_X = c_{X1} + \sum_{j=1}^{N_d} S_{x,j1} c_{d,j} \tag{88}$$

The values of N_X, c_x and S_x are as follows: $N_X = 1$, $c_{x1} = c_X$, $S_{x,j1} = S_{x,,X}$

2.2.5. Dissolution and precipitation of minerals

2.2.5.1. Equilibrium approach

Under equilibrium conditions, dissolution-precipitation reactions can be described by the Law of Mass Action which states that

$$X_m \lambda_m K_m = \prod_{i=1}^{N_c} c_i^{\nu_{mi}^p} \gamma_i^{\nu_{mi}^p} \tag{89}$$

where X_m is the molar fraction of the m-th solid phase, λ_m is its thermodynamic activity coefficient (X_m and λ_m are taken equal to 1 for pure phases), c_i and γ_i are the concentration and activity coefficient of the i-th species, ν^p_{mi} its stoichiometric coefficient in the dissolution reaction of the m-th solid phase, and K_m is the corresponding equilibrium constant.

The saturation ratio is the ratio between the ion activity product and the solubility product:

$$\Omega_m = \frac{1}{K_m} \prod_{i=1}^{N_C} a_i^{\nu_{mi}^p} \tag{90}$$

The log Ω_m value is known as the saturation index SI_m. The system reaches the minimun free energy at equilibrium when $\Omega_m = 1$ or $SI_m = 0$. Saturation ratios Ω_m greater than 1

($SI_m > 0$) indicate that the system will evolve so that the m-th mineral precipitates. On the contrary, when $\Omega_m < 1$ ($SI_m < 0$) the mineral will tend to dissolve. This means that the mineral phases that can participate are those already present initially plus other potential minerals having Ω_m values greater than 1. However, the phase rule states that at given pressure and temperature the number of phases cannot exceed the number of components N_C. In such cases, only the minerals having the largest Ω_m values are retained as phases. Similarly, when a mineral being dissolved is exhausted it must be excluded from the list of mineral phases.

2.2.5.2. kinetic Approach

Kinetic rate laws

The thermodynamic chemical equilibrium condition only states the minimum energy state of the system, but says nothing about the progress of the system. Kinetics offers a way to analyze the chemical evolution of a reaction and allows incorporating explicitly the time variable.

Some geochemical processes (such as dissolution and precipitation of many minerals) are known to progress so slowly that they may never reach equilibrium. In these cases the kinetic law is required. However, quantitative information on the kinetic law of most natural processes is scarce, although significant progress has been made during the last years on dissolution rates. In RCB the rates for mineral precipitation are assumed to follow the same law as dissolution.

There are several experimental expressions for dissolution rate in the literature. It is common to express the rate as the addition of several terms, each one expressing the dependence of the rate upon a particular species in solution (see for example Chou et al., 1989):

$$r_m = \sigma_m \sum_{k=1}^{N_k} k_{mk} c_k \tag{91}$$

where N_k is the number of terms of the experimental expression, c_k the concentration of the kth species in solution, k_{mk} an experimental constant and σ_m the reactive surface (surface of mineral per volume of rock).

For mineral dissolution, Lasaga et al., (1994) have proposed the following general expression

$$r_m = \sigma_m k_m \prod_{i=1}^{N_S} a_{m,i}^{p_{m,i}} \left(\Omega_m^{\theta} - 1\right)^{\eta} \tag{92}$$

where r_m is the mineral dissolution rate (moles of mineral per volume of rock and unit time), k_m is the experimental rate constant (in the same units), Ω_m is the ratio between the ion activity product and the equilibrium constant as defined in Eqn. (90). The parameters θ and η must be determined from experiments; usually but not always they are taken equal to 1. The term inside the parenthesis, called the far-from-equilibrium

function, decreases the reaction rate in a non-linear way, as the solution approaches to equilibrium. The term a_i^{pi} accounts for the catalytic effect of some species (particularly of H^+), where the value of p_i is determined experimentally.

Rate constants are usually obtained by means of laboratory experiments carried out at conditions far from equilibrium. They depend on temperature according to the Arrhenius equation:

$$k_m = k_0 \exp\left(\frac{-E_{a,m}}{RT}\right) \tag{93}$$

where k_0 is a constant and $E_{a,m}$ is the apparent activation energy of the overall reaction process, which for most minerals range from 30 to 80 kJ/mol (Lasaga, 1984). Both k_0 and $E_{a,m}$ are determined from experiments performed at different temperatures.

According to the previous discussion RCB uses a general formulation which includes several types of experimental functions:

$$r_m = \sigma_m \zeta_m \exp\left(\frac{E_{a,m}}{RT}\right) \sum_{k=1}^{N_k} k_{mk} \prod_{i=1}^{N_S} a_i^{p_{mki}} \left(\Omega_m^{\theta_{mk}} - 1\right)^{\eta_{mk}} \tag{94}$$

Factor ζ_m takes on values of +1 or -1 depending on whether Ω_m is larger or smaller than 1 (precipitation or dissolution), respectively. At equilibrium $\Omega_m = 1$, and therefore $r_m=0$.

Another formulation, that permits RCB, is based on Monod and includes *p*-order, catalysis and inhibition factors:

$$r_m = \sigma_m \prod_{k=1}^{N_k} f_{mk} \tag{95}$$

where f_{mk} is a term which can be one of the three following types:

p-order
$$f_{mk} = k_{mk} \prod_{i=1}^{N_s} c_i^{p_{mki}} \tag{96}$$

Catalysis
$$f_{mk} = \frac{\prod_{i=1}^{N_s} c_i^{p_{mki}}}{k_{mk} + \prod_{i=1}^{N_s} c_i^{p_{mki}}} \tag{97}$$

Inhibition
$$f_{mk} = \frac{k_{mk}}{k_{mk} + \prod_{i=1}^{N_s} c_i^{p_{mki}}} \tag{98}$$

Reactive surface

The reactive surface (σ_m) changes when the mineral precipitates or dissolves and, hence, can be written as a function of the concentration of the mineral (c_m). RCB assumes the minerals to have the shape of spherical grains. Then the reactive surface is:

$$\sigma_m = 4\pi r_g^2 n_g \tag{99}$$

where r_g is the radius of a grain and n_g is the number of grains per volume of rock. The concentration of the mineral can be written as:

$$c_m = \frac{4}{3}\frac{\pi r_g^3 n_g}{V_m} \tag{100}$$

where V_m is the molar volume of a mineral. By solving r_g from (100) and substituting it into (99), we obtain:

$$\sigma_m = \left(36\pi n_g\right)^{1/3}\left(V_m c_m\right)^{2/3} = k_g c_m^{2/3} \tag{101}$$

where k_g is a geometrical constant. Therefore, the reactive surface at a time t can be calculated from an initial reactive surface (σ_m^0) and initial mineral concentration (c_m^0):

$$\sigma_m = \left(\frac{c_m}{c_m^0}\right)^{2/3}\sigma_m^0 \tag{102}$$

When the initial mineral concentration (c_m^0) equals zero, equation (102) cannot be applied. In that case, RCB assumes an initial radius (r_g^0) of 10^{-8} m and calculates the reactive surface by first calculating the number of grains per volume (n_g) from the initial reactive surface (σ_m^0) and the initial radius (r_g^0) and then substituting n_g into equation (101). This leads to:

$$\sigma_m = \frac{\left(9\sigma_m^0\right)^{1/3}}{\left(r_g^0\right)^{2/3}}\left(V_m c_m\right)^{2/3} \tag{103}$$

Note that the initial reactive surface (σ_m^0) is not zero, contrary to the mineral concentration (c_m^0).

2.2.6. Gas liquid interactions

RCB assumes that all gas-liquid reactions are sufficiently fast with respect to flow to reach equilibrium. For reactions involving aqueous and gaseous phases the mass action law states that

$$p_f \gamma_f K_f = \prod_{i=1}^{N_C} c_i^{\nu_{fi}} \gamma_i^{\nu_{fi}} \tag{104}$$

where p_f is the partial pressure of the f-th species in the gas phase, γ_f is its activity coefficient, c_i and γ_i are the concentration and activity coefficient of the i-th dissolved primary species, respectively, ν_{fi} is the stoichiometric coefficient of the i-th species in the exsolution reaction of fluid f, and K_f is the equilibrium constant of the reaction.

For low pressures (in the range of atmospheric pressure), the gaseous phase behaves like an ideal mixture (γ_f = 1). Then, the chemical equilibrium between a species in the aqueous phase and in the gas phase can be represented by Henry's law:

$$p_f = \frac{\gamma_a}{K_f} c_a \tag{105}$$

where the fraction is the so called Henry's constant, which has units of (bar kg_{water}/mol) and depends on the ionic strength of the solution. Moreover, the partial pressure p_f is equal to the total pressure times the molar fraction X_f (Dalton's law). The sum of the partial pressures (p_f) of all gaseous species equals the pressure of the gas phase (P_g):

$$P_g = \sum_f p_f \tag{106}$$

At low pressures, not only the mixture behaves as ideal, but also each species respects the ideal gas equation:

$$p_f V = n_f RT \tag{107}$$

so that we can write the concentration of the chemical species in the gas phase (c_f), expressed in moles per unit of volume, as:

$$c_f = \frac{p_f}{RT} \tag{108}$$

2.3. Reactive transport

2.3.1. Mass balances

RCB uses the mathematical formulation for reactive transport of Saaltink et al. (1998), to which we added terms for the transport and chemistry of gaseous species. Then, the mass balance of reactive transport can be written as:

$$\mathbf{U_a}\frac{\partial \phi S_l \rho_l \mathbf{c_a}}{\partial t}+\mathbf{U_d}\frac{\partial \phi \rho_l \mathbf{c_d}}{\partial t}+\mathbf{U_m}\frac{\partial (1-\phi)\rho_s \mathbf{c_m}}{\partial t}+\mathbf{U_g}\frac{\partial \frac{\phi S_g}{RT}\mathbf{p_f}}{\partial t}=$$
$$=\mathbf{U_a}L_l(\mathbf{c_a})+\mathbf{U_f}L_g(\mathbf{p_f})+\mathbf{U}\mathbf{S}_\mathbf{k}^t\mathbf{r_m}(\mathbf{c_a}) \quad (109)$$

Equations (109) are the N_c overall reactive transport equation. Vectors $\mathbf{c_a}$, $\mathbf{c_d}$, $\mathbf{c_m}$ (mol kg^{-1}) and $\mathbf{p_f}$ (Pa) are the concentrations of aqueous species, adsorbed species, minerals and partial pressures of gaseous species, respectively. Matrix $\mathbf{S_k}$ and vector $\mathbf{r_k}$ contains the stoichiometric coefficients and the rates of the kinetic reactions, which can be considered as functions of all aqueous concentrations. Matrices $\mathbf{U_a}$, $\mathbf{U_d}$, $\mathbf{U_m}$ and $\mathbf{U_g}$ are called the component matrices for aqueous, sorbed, mineral and gaseous species and relate the concentrations of the species with the total concentrations of the components. The matrix $\mathbf{U}$ is the component matrix for all species. These matrices can be computed from the stoichiometric coefficient of the chemical reactions. An exception are columns of these matrices that refer to the electron (e^-) involved in redox reactions. The use of e^- stems from writing a redox reaction as two half-reactions. This is useful for mass action laws, but in reality there is no free electron in the solution (its real concentration equals zero). Therefore, the columns of the component matrix that refer to the electron must be set to zero.

By using mineral equilibrium equations we can eliminate N_m of the N_c transport equations as explained in more detail by Saaltink et al. (1998). This is achieved by multiplying equations by matrix $\mathbf{E}$, kernel of $\mathbf{U_m}$ (i.e., $\mathbf{EU_m} = \mathbf{0}$). This eliminates the concentrations of minerals in equilibrium and reduces the number of transport equations per node to N_c - N_m. The resulting transport equations are denoted:

$$\mathbf{EU_a}\frac{\partial \phi S_l \rho_l \mathbf{c_a}}{\partial t}+\mathbf{EU_d}\frac{\partial (1-\phi)\rho_s \mathbf{c_d}}{\partial t}+\mathbf{EU_g}\frac{\partial \frac{\phi S_g}{P_g}\mathbf{p_f}}{\partial t}=$$
$$=\mathbf{EU_a}L_l(\mathbf{c_a})+\mathbf{EU_g}L_g(\mathbf{p_f})+\mathbf{EU}\mathbf{S}_\mathbf{k}^t\mathbf{r_k}(\mathbf{c_a}) \quad (110)$$

As explained in chapter 2.2 the variables $\mathbf{c_a}$, $\mathbf{c_d}$ and $\mathbf{p_f}$ can be written as function of N_c - N_m primary variables $\mathbf{c_i}$.

L_l and L_g are linear operators for the advection, dispersion/diffusion and non-chemical sink-source terms for the liquid and gas phase, respectively:

$$L_l() = -\nabla\cdot\left(\mathbf{q_l}\rho_l()\right)+\nabla\cdot\left(\mathbf{D_l}\phi S_l \rho_l \nabla()\right)+m_l \quad (111)$$

$$L_g() = -\nabla\cdot\left(\mathbf{q_g}\frac{1}{RT}()\right)+\nabla\cdot\left(\mathbf{D_g}\phi S_g \frac{P_g}{RT}\nabla\frac{()}{P_g}\right)+m_g \quad (112)$$

where m_l and m_g are the non-chemical sources-sinks (mol m^{-3} s^{-1}) and $\mathbf{D_l}$ and $\mathbf{D_g}$ are the dispersion/diffusion tensors (m^2 s^{-1}). In two dimensions these tensors are:

$$\mathbf{D}_{\boldsymbol{\alpha}} = \begin{pmatrix} \dfrac{\alpha_{L,\alpha} v_{x,\alpha}^2 + \alpha_T v_{y,\alpha}^2}{|\mathbf{v}_{\boldsymbol{\alpha}}|} & \dfrac{(\alpha_{L,\alpha} - \alpha_{T,\alpha}) v_{x,\alpha} v_{y,\alpha}}{|\mathbf{v}_{\boldsymbol{\alpha}}|} \\ \dfrac{(\alpha_{L,\alpha} - \alpha_{T,\alpha}) v_{x,\alpha} v_{y,\alpha}}{|\mathbf{v}_{\boldsymbol{\alpha}}|} & \dfrac{\alpha_{L,\alpha} v_{y,\alpha}^2 + \alpha_{T,\alpha} v_{x,\alpha}^2}{|\mathbf{v}_{\boldsymbol{\alpha}}|} \end{pmatrix} + \mathbf{I} D_{0,\alpha} \tau_\alpha \qquad (113)$$

where subscript α refers to the phase (l or g). For one dimension equation (113) reduces to:

$$\mathbf{D}_{\boldsymbol{\alpha}} = \alpha_{L,\alpha} v_{x,\alpha} + D_{0,\alpha} \tau_\alpha \qquad (114)$$

where α_L and α_T are the longitudinal and transversal dispersivities (m), $v_{x,\alpha}$ and $v_{y,\alpha}$ are the velocities (m s^{-1}) in x and y direction for phase α, D_0 is the molecular diffusion (m^2 s^{-1}) in the pure phase and τ is the tortuosity. RCB permits two functions to calculate the tortuosity, τ:

$$\tau = \sqrt{\phi S} \qquad (115)$$

$$\tau = \frac{(\phi S)^{\frac{7}{3}}}{\phi^2} \qquad (116)$$

The first term of the right-hand-sides of (113) and (114) represents dispersion and the second molecular diffusion. It is worth noting that, generally, in the liquid phase the dispersive term dominates, whereas in the gas phase the diffusive term dominates. The most correct would be to calculate the diffusion in the gas phase according to complex relations taking into account pressure, temperature, type of gaseous species and chemical composition of the gas as explained by Thorstenson and Pollock (1989), Baehr and Baker (1995) and Abu-El-Sha'r and Abriola (1997). We opted for calculating the gaseous diffusion coefficient, D_0, by assuming binary diffusion between every gaseous species and a majority species (usually N_2). Then the diffusion coefficient for gaseous species ($D_{0,g}$) becomes:

$$D_{0,g} = \frac{1.43 \cdot 10^{-8} T^{1.75}}{P_g \sqrt{2\left(w_i^{-1} + w_m^{-1}\right)^{-1}} \left(a_i^{\frac{1}{3}} + a_m^{\frac{1}{3}} \right)^2} \qquad (117)$$

where w is the molecular weight in g/mole, a is the diffusion volume. Subscripts i and m refer to the considered gaseous species and the majority species. Diffusion coefficient, $D_{0,g}$, gas pressure, P_g, and temperature, T, are in m^2/s, Pa and K, respectively.

2.3.2. Boundary conditions

Boundary conditions and expressions for the non-chemical sources-sinks terms (m_l and m_g in equations (111) and (112)) have to be written for mass the mass balance equation for every chemical component and every mobile phase (that is, liquid and gas).

RCB permits two types of boundary conditions. In the first type, a component mass flux is calculated by multiplying the boundary flux of a phase (liquid, j_l, or gas, j_g, see chapter 2.1.3 and 2.1.4) by a total concentration of a component, which is that of the node of the boundary (u_a or u_g) or an externally specified one ($(u_a)^0$ or $(u_g)^0$), depending on whether the phase enters or leaves the medium:

$$\begin{aligned} m_l &= j_l\left(u_a\right)^0 \quad & j_l > 0 \\ m_l &= j_l u_a \quad & j_l < 0 \end{aligned} \tag{118}$$

$$\begin{aligned} m_g &= j_g\left(u_g\right)^0 \quad & j_g > 0 \\ m_g &= j_g u_g \quad & j_g < 0 \end{aligned} \tag{119}$$

The second one is a mixed condition according to the following expressions:

$$m_l = \gamma_l\left(\left(u_a\right)^0 - u_a\right) \tag{120}$$

$$m_g = \gamma_g\left(\left(u_g\right)^0 - u_g\right) \tag{121}$$

where γ_l and γ_g are leakage coefficients. A fixed concentration can be simulated by giving these leakage coefficient very high values (but no to high to avoid numerical instabilities). It is worth mentioning that the first type is more apt for advection dominated cases, whereas a fixed concentration is more apt for diffusion dominated cases.

The values of the external total concentrations ($(u_a)^0$ or $(u_g)^0$) must be given for every component. For the aqueous phase, RCB first calculates the concentrations of the primary species by imposing to each component one of the equations explained in table 1. Then it calculates the total aqueous concentrations by equation (44).

Option	Equation
Total aqueous component	$(u_a)^0 = \text{fixed}$
Charge balance	$\sum_i z_i (c_{ai})^0 = 0$
Activity	$(a)^0 = \text{fixed}$
Equilibrium with mineral	$(\Omega_m)^0 = 1$
Equilibrium with gas	$(p_f)^0 = \text{fixed}$

Table 1. Options for calculating the chemical composition of the boundary.

For the gas phase the partial pressure of each gaseous species must be given, from which the total gas concentration for each component ($(u_g)^0$) is calculated.

2.4. Effects of Reactive Transport on Thermohydraulics

Reactive transport properties can also affect the thermohydraulic problem. RCB can model the effect of dissolution and precipitation on porosity and permeability and the effect of aqueous solutes on certain flow properties These effects are modelled through a simple time lagged approach (i.e., no iteration is performed between thermo hydraulics and reactive transport).

The change in porosity ($\Delta\phi$) is calculated from the change in the concentrations of the minerals (Δc_m) through:

$$\Delta\phi = -\sum_i V_{m,i} \Delta c_{m,i} \tag{122}$$

where V_m is the molar volume of a mineral. The intrinsic permeability may depend on the porosity through the Kozeny model (see chapter 3.2).

The following hydraulic constitutive laws are effected by the mass fraction of aqueous solutes (mass of solute per mass of liquid, ω^h_l): the surface tension (σ) of the retention curve (see chapter 3.1), the liquid density and the liquid viscosity (chapter 3.9). The solute mass fraction is calculated from the aqueous solute concentrations (c_a in mol/kg of water) as:

$$\omega_l^h = \frac{\sum_i c_{ai} M_i}{1 + \sum_i c_{ai} M_i} \tag{123}$$

where M_i is the molecular weight.

Moreover, the vapour density (see chapter 3.12) is affected by the water activity (a_w), This activity is assumed to be the molar fraction of water in liquid. Therefore it can be calculated from the aqueous solute concentrations:

$$a_w = \frac{1}{1 + M_w \sum_i c_{ai}} \tag{124}$$

where M_w is the molecular weight of water.

3. Thermohydraulic constitutive laws

In this chapter a list is given of all thermohydraulic constitutive laws that can be used in RCB. At the same time it explains the meaning of PARCL of the general input file (cardgroup 16, chapter 4.2).

3.1. Retention curve

CODES	ICL=6, ITYCL=see below
DESCRIPTION	Curve capillary pressure versus degree of saturation.
EQUATIONS	ITYCL=1: Van Genuchten model (van Genuchten, 1980): $$S_e = \frac{S_l - S_{rl}}{S_{ls} - S_{rl}} = \left(1 + \left(\frac{P_g - P_l}{P}\right)^{\frac{1}{1-\lambda}}\right)^{-\lambda}$$ $$P = P_o \frac{\sigma}{\sigma_o}$$ ITYCL=2: Linear model: $$S_e = \frac{S_l - S_{rl}}{S_{ls} - S_{rl}} = 1 - \frac{P_g - P_l}{P_o}$$ ITYCL=4: Square law: $$S_e = \frac{S_l - S_{rl}}{S_{ls} - S_{rl}} = \frac{1}{\sqrt{1 + \frac{P_g - P_l}{P_o}}}$$ ITYCL=9: Van Genuchten model with assimptotic branch that goes to negative capillary pressures. $$S_e = \frac{S_l - S_{rl}}{S_{ls} - S_{rl}} = \left(1 + \left(\frac{P_g - P_l}{P}\right)^{\frac{1}{1-\lambda}}\right)^{-\lambda} \quad P_g - P_l > a = \frac{P_o}{f}$$ $$P = P_o \frac{\sigma}{\sigma_o}$$ $$S_l = S_{ls} - \frac{b}{\left(P_g - P_l - a - c\right)^2} \qquad P_g - P_l < a$$ For the van Genuchten models (ITYCL=1 or 9) the surface tension (σ) is calculated as (Horvath, 1985):

	$\sigma = 0.03059 \exp\left(\dfrac{252.93}{273.15+T}\right) + 0.04055\omega_l^h$ N/m

PARAMETERS FOR ITYCL=1

P1	P_o	MPa	Measured P at certain temperature
P2	σ_o	N m^{-1}	Surface tension at temperature in which P_o was measured (usually σ_o=0,072 N/m at 20ºC)
P3	λ		Shape function for retention curve
P4	S_{rl}		Residual saturation
P5	S_{ls}		Maximum saturation
P6	ϕ_o		Reference porosity for porosity influence on retention curve
P7			
P8	a		Parameter for porosity influence on retention curve: $P_o(\phi)=P_o \exp(a(\phi_o-\phi)$
P9	b		Parameter for porosity influence on retention curve: $\lambda(\phi)= \lambda \exp(b(\phi_o-\phi))$

PARAMETERS FOR ITYCL=2

P1	P_o	MPa	Measured P at certain temperature
P2	Void		
P3	Void		
P4	S_{rl}		Residual saturation
P5	S_{ls}		Maximum saturation

PARAMETERS FOR ITYCL=4

P1	P_o	MPa	Measured P at certain temperature
P2	Void		
P3	Void		
P4	S_{rl}		Residual saturation
P5	S_{ls}		Maximum saturation

PARAMETERS FOR ITYCL=9

P1	P_o	MPa	Measured P at certain temperature
P2	σ_o	N m^{-1}	Surface tension at temperature in which P_o was measured (usually σ_o=0,072 N/m at 20ºC)
P3	λ		
P4	S_{rl}		Residual saturation
P5	S_{ls}		Maximum saturation
P6	f		Used for the asymptotic branch

S_{rl} and S_{ls} are lower and upper bounds of saturation. Effective saturation S_e is defined in such a way that ranges between 0 and 1.

If hysteretic behaviour is allowed (IOPTHYS=1 is necessary), the above parameters are considered to belong to the dry retention curve and some additional parameters are necessary in order to define the transition and the wetting paths:

P6	P_{ow}	MPa	P_o for wetting branch
P7	dS_e		Effective degree of saturation transition interval
P8	s_d	MPa	Maximum suction in soil history
P9	s_w	MPa	Minimum suction in soil history
P10	λ_w		λ for wetting branch

3.2. Intrinsic permeability

CODES	ICL=7, ITYCL=1
DESCRIPTION	Intrinsic permeability
EQUATIONS	For a continuum medium (Kozeny's model): $\mathbf{k} = \mathbf{k}_o \frac{\phi^3}{(1-\phi)^2} \frac{(1-\phi_o)^2}{\phi_o^3}$ ϕ_o : reference porosity $\mathbf{k}_o$: intrinsic permeability for matrix ϕ_o which is used in Darcy's law (Bear, 1972): $\mathbf{q}_\alpha = -\frac{\mathbf{k} k_{r\alpha}}{\mu_\alpha}\left(\nabla P_\alpha - \rho_\alpha \mathbf{g}\right)$ where viscosity, density and relative permeability are defined in other laws.

PARAMETERS:

P1	$(k_{11})_o$	m^2	Intrinsic permeability, 1st principal direction
P2	$(k_{22})_o$	m^2	Intrinsic permeability, 2nd principal direction
P3	$(k_{33})_o$	m^2	Intrinsic permeability, 3rd principal direction
P4	ϕ_o		Reference porosity for read intrinsic permeability. If ϕ_o=0, permeability will be constant.
P5	ϕ_{min}		Minimum porosity, porosity will not be lower than this value

3.3. Liquid phase relative permeability

CODES	ICL=14 ITYCL= see below

DESCRIPTION	By default, the consistent form of relative permeability with van Genuchten model is used. In this case, this ICL=14 can be ignored.
EQUATIONS	ITYCL=1: van Genuchten model $k_{rl} = \sqrt{S_e}\left(1-\left(1-S_e^{1/\lambda}\right)^{\lambda}\right)^2$ ITYCL=5: Liquid perfectly mobile $k_{rl} = 1$ ITYCL=6: Generalised power $k_{rl} = AS_e^{\lambda}$ ITYCL=8: Power with initial cut off $k_{rl} = A\left(\dfrac{S_e - S_{eo}}{1-S_{eo}}\right)^{\lambda} \qquad S_e >= S_{eo}$ $k_{rl} = 0 \qquad$ otherwise

PARAMETERS FOR ITYCL=1

P1	Void		
P2	Void		
P3	λ		Power
P4	S_{rl}		Residual saturation (default = same value as for retention curve)
P5	S_{ls}		Maximum saturation (default = same value as for retention curve)

PARAMETERS FOR ITYCL=5
None

PARAMETERS FOR ITYCL=6

P1	Void		
P2	A		constant
P3	λ		Power (typically 3)
P4	S_{rl}		residual saturation (default = same value as for retention curve)
P5	S_{ls}		maximum saturation (default = same value as for retention curve)

PARAMETERS FOR ITYCL=8:

P1	S_{eo}		Parameter
P2	A		Constant
P3	λ		Power
P4	S_{rl}		Residual saturation (default = same value as for retention curve)
P5	S_{ls}		Maximum saturation (default = same value as for retention curve)

S_{rl} and S_{ls} are lower and upper bounds of saturation. Effective saturation S_e is defined in such a way that ranges between 0 and 1. In principle, the same values S_{rl} and S_{ls} should be defined for liquid and gas relative permeability and for retention curve. However, different values can be used to define a maximum saturation of liquid with possibility of remanent gas flow or *vice-versa*.

3.4. Gas phase relative permeability

CODES	ICL=19 ITYCL= see below
DESCRIPTION	Relative permeability of the gas phase
EQUATIONS	ITYCL=1: Default law $k_{rg} = 1 - k_{rl}$ ITYCL=5: Gas perfectly mobile $k_{rg} = 1$ ITYCL=6: Generalised power $k_{rg} = A S_{eg}{}^{\lambda}$

PARAMETERS FOR ITYCL=1

P1	Void		
P2	Void		
P3	Void		
P4	S_{rg}	-	Residual saturation (default = 1-S_{ls} in retention curve)
P5	S_{gs}	-	Maximum saturation (default = 1-S_{rl} in retention curve)

PARAMETERS FOR ITYCL=6

P1	Void		
P2	A		Constant
P3	λ		Power
P4	S_{rg}		Residual saturation (default = 1-S_{ls} in retention curve)
P5	S_{gs}		Maximum saturation (default = 1-S_{rl} in retention curve)

3.5. Diffusive fluxes of mass

CODES	ICL=11, 12 and 13. ITYCL=1, 2
DESCRIPTION	Diffusion coefficients
EQUATIONS	Fick's law for molecular diffussion is written as:

	$\mathbf{i}_\alpha^i = -\left(\tau\phi\rho_\alpha S_\alpha D_m^i \mathbf{I}\right)\nabla\omega_\alpha^i$ where ϕ is porosity, ρ_α is density, S_α is degree of saturation, ω is mass fraction and D_m^i is the diffusion coefficient of species i in phase α in m^2/s. The nonadvective flux of a species in a phase is composed by molecular diffusion and mechanical dispersion (dispersion is defined in another set of parameters). ICL=11. ITYCL=1. Molecular diffusion of vapour: $D_m^{vapor} = D\left(\frac{\left(273.15+T\right)^n}{P_g}\right)$ where P_g is the gas pressure in Pa, and D and n are parameters. Tortuosity is defined as a constant value in this case: $\tau = \text{constant}=\tau_0$ ICL=11. ITYCL=2. Molecular diffusion of vapour (Pollock, 1986): $D_m^{vapor} = D\left(\frac{\left(273.15+T\right)^n}{P_g}\right)$ where P_g is the gas pressure in Pa, and D and n are parameters. Tortuosity is defined in this case as: $\tau = \tau_0\left(S_g\right)^m$ where τ_0 and m are parameters. ICL=12. ITYCL=1. Molecular diffusion of dissolved salt and dissolved air: $D_m^{\text{air or solute}} = \tau D\exp\left(\frac{-Q}{R\left(273.15+T\right)}\right)$

PARAMETERS FOR ICL=11, ITYCL=1

P1	D	$m^2\ s^{-1}\ K^{-n}$ Pa	Default=5.9 10^{-6} (default value).
P2	n		Default=2.3 (default value).
P3	τ_0		Coefficient of tortuosity, default=1.0
P4	Void		
P5	Void		

PARAMETERS FOR ICL=11, ITYCL=2

P1	D	$m^2\ s^{-1}\ K^{-n}$ Pa	Default=5.9 10^{-6} (default value).
P2	n		Default=2.3 (default value).
P3	τ_o		Parameter for coefficient of tortuosity, default=1.0
P4	m		Power for tortuosity function of saturation.
P5	Void		

PARAMETERS FOR ICL=12, ITYCL=1

P1	D	$m^2\ s^{-1}$	Default=1.1 10^{-4} (default value).

P2	Q	J mol^{-1}	Default=24530 (default value).
P3	τ		Coefficient of tortuosity, default=1.0
P4	Void		
P5	Void		

3.6. Dispersive fluxes of mass and energy

CODES	ICL=8 ITYCL=1
DESCRIPTION	Dispersivities for vapour, dissolved air and heat.
EQUATIONS	Mechanical dispersion mass flux is computed by means Fick's law written as: $\mathbf{i}_\alpha^i = -\left(\rho_\alpha \mathbf{D'}_\alpha\right)\nabla\omega_\alpha^i$ where the mechanical dispersion tensor is defined as: $\mathbf{D'}_\alpha = d_t \lvert\mathbf{q}_\alpha\rvert \mathbf{I} + (d_l - d_t)\frac{\mathbf{q}_\alpha \mathbf{q}_\alpha^t}{\lvert\mathbf{q}_\alpha\rvert}$ where d_l is longitudinal dispersivity and d_t is transversal dispersivity. Mechanical dispersion heat flux is computed by means Fourier's law written as: $\mathbf{i}_h = -\left(c_\alpha \rho_\alpha \mathbf{D'}_\alpha\right)\nabla T$ where $c_{\square}$ is the specific heat of the phase, and the mechanical dispersion tensor is defined in the same way as before but using the corresponding dispersivities for heat dispersion (only the contribution due to liquid phase dispersion, i.e. $=l$ has been implemented). Heat conduction is defined in another set of variables.

PARAMETERS FOR ICL=8 AND ITYCL=1

P1	d_l	m	Longitudinal dispersivity for solutes in liquid phase
P2	d_t	m	Transverse dispersivity for solutes in liquid phase
P3	Void		
P4	d_l	m	Longitudinal dispersivity for heat
P5	d_t	m	Transverse dispersivity for heat
P6	d_l	m	Longitudinal dispersivity for vapour, default: P1
P7	d_t	m	Transverse dispersivity for vapour, default: P2

3.7. Conductive flux of heat

CODES	ICL=9 and 20
DESCRIPTION	ICL=9: Dependence on porosity and temperature. ICL=20: Dependence on water content.
EQUATIONS	Thermal conductivity is used in Fourier's law to compute conductive heat flux, i.e.: $\mathbf{i}_c = -\lambda \nabla T$ There are two possibilities to solve conductive flux of heat through this law (ICL=9): Giving directly λ_{dry} and λ_{sat}. These values can be measured in the laboratory. They will be used in law ICL=20. Giving the conductivity of the phases of the soil, i.e. $(\lambda_{solid})_o$, λ_{liquid} λ_{gas} and a_1, a_2, a_3. In this case, λ_{dry} and λ_{sat} are calculated according to the laws given below. ICL=9. ITYCL=1: Thermal conductivity dependence on porosity. Geometric weighted mean. $\lambda_{dry} = \lambda_{solid}^{(1-\phi)} \lambda_{gas}^{\phi}$ $\quad$ $\lambda_{sat} = \lambda_{solid}^{(1-\phi)} \lambda_{liq}^{\phi}$ $\lambda_{solid} = (\lambda_{solid})_o + a_1 T + a_2 T^2 + a_3 T^3$ ICL=9. ITYCL=2: Thermal conductivity dependence on porosity. Weighted arithmetic mean. $\lambda_{dry} = (1-\phi)^n \lambda_{solid} + \phi^n \lambda_{gas}$ $\quad$ $\lambda_{sat} = (1-\phi)^n \lambda_{solid} + \phi^n \lambda_{liq}$ ICL=9. ITYCL=3: Thermal conductivity dependence on porosity. Nonlinear function of porosity. $\lambda_{dry} = \lambda_{solid} + \left(\lambda_{odry} - \lambda_{solid}\right)\left(\dfrac{\phi}{\phi_o}\right)^n$ $\lambda_{sat} = \lambda_{solid} + \left(\lambda_{osat} - \lambda_{solid}\right)\left(\dfrac{\phi}{\phi_o}\right)^n$ Dependence of thermal conductivity on degree of saturation can be considered in the following ways: ICL=20. ITYCL=1: $\lambda = \lambda_{sat}\sqrt{S_l} + \lambda_{dry}\left(1-\sqrt{S_l}\right)$ ICL=20. ITYCL=2: $\lambda = \lambda_{sat}^{S_l} \lambda_{dry}^{(1-S_l)}$ (parameters are not necessary for ICL=20 and ITYCL=1 and ITYCL=2)

PARAMETERS FOR ICL=9, ITYCL=1

P1	λ_{dry}	W mK^{-1}	Thermal conductivity of the dry porous medium
P2	λ_{sat}	W mK^{-1}	Thermal conductivity of the water saturated porous medium

P3	$(\lambda_{solid})_o$	W mK^{-1}	Solid phase thermal conductivity (ignored if λ_{dry}, $\lambda_{sat} > 0$)
P4	λ_{gas}	W mK^{-1}	Gas phase thermal conductivity (ignored if λ_{dry}, $\lambda_{sat} > 0$)
P5	λ_{liq}	W mK^{-1}	Liquid phase thermal conductivity (ignored if λ_{dry}, $\lambda_{sat} > 0$)
P6	a_1		Ignored if λ_{dry}, $\lambda_{sat} > 0$
P7	a_2		Ignored if λ_{dry}, $\lambda_{sat} > 0$
P8	a_3		Ignored if λ_{dry}, $\lambda_{sat} > 0$
P9	Void		
P10	Void		

PARAMETERS FOR ICL=9, ITYCL=2

P1	λ_{dry}	W mK^{-1}	Thermal conductivity of the dry porous medium
P2	λ_{sat}	W mK^{-1}	Thermal conductivity of the water saturated porous medium
P3	$(\lambda_{solid})_o$	W mK^{-1}	Solid phase thermal conductivity (ignored if λ_{dry}, $\lambda_{sat} > 0$)
P4	λ_{gas}	W mK^{-1}	Gas phase thermal conductivity (ignored if λ_{dry}, $\lambda_{sat} > 0$)
P5	λ_{liq}	W mK^{-1}	Liquid phase thermal conductivity (ignored if λ_{dry}, $\lambda_{sat} > 0$)
P6	a_1		Ignored if λ_{dry}, $\lambda_{sat} > 0$
P7	a_2		Ignored if λ_{dry}, $\lambda_{sat} > 0$
P8	a_3		Ignored if λ_{dry}, $\lambda_{sat} > 0$
P9	Void		
P10	n		Power of porosity function

PARAMETERS FOR ICL=9. ITYCL=3.

P1	Void		
P2	Void		
P3	$(\lambda_{solid})_o$	W mK^{-1}	Solid phase thermal conductivity
P4	$(\lambda_{dry})_o$	W mK^{-1}	Dry thermal conductivity for reference porosity
P5	(λ_{sat})	W mK^{-1}	Saturated thermal conductivity for reference porosity.
P6	Void		
P7	Void		
P8	Void		
P9	ϕ_o		Reference porosity
P10	n		Power of porosity

Heat dispersion is defined in the constitutive law ICL=8, ITYCL=1 (Dispersive fluxes of mass and energy).

3.8. Solid phase properties

CODES	ICL=10 ITYCL=1, 2
DESCRIPTION	Solid specific heat, density and expansion coeficient
EQUATIONS	

PARAMETERS FOR ITYCL=1

P1	C_s	J kg^{-1} K^{-1}	Solid phase specific heat (default: 874)
P2	ρ_s	kg m^{-3}	Solid phase density (default: 2163)
P3	α_s	$^oC^{-1}$	Linear thermal expansion coefficient for grains (not volumetric).
P4	T_o	^oC	Reference temperature for thermal expansion (default: 40)
P5			

PARAMETERS FOR ITYCL=2

P1	c_s	J kg^{-1} K^{-1}	Solid phase specific heat for *T=0* (default: 874)
P2	ρ_s	kg m^{-3}	Solid phase density (default: 2163)
P3	α_s	$^oC^{-1}$	Linear thermal expansion coefficient for grains (not volumetric)
P4	T_o	^oC	Reference temperature for thermal expansion
P5	*Void*		
P6	dc_s/dt		Variation of solid phase specific heat

Linear thermal dilatance coefficient for grains should be identical to the bulk value if thermal expansion of the porous medium does not produce porosity variations. Specific heat for water, air and salt (not solid) are internal values.

3.9. Liquid phase properties

CODES	ICL=15 and 16
DESCRIPTION	ICL=15, Liquid density. ICL=16. Liquid viscosity.
EQUATIONS	ICL=15, ITYCL=1 $\rho_l = \rho_{l0} \exp(\beta(P_l - P_{lo}) + \alpha T + \gamma\omega_l^h)$ ICL=15, ITYCL=2 $\rho_l = \rho_{l0}(1 + \beta(P_l - P_{lo}) + \alpha T + \gamma\omega_l^h)$ ICL=16, ITYCL=1 (Hassanizadeh and Leijnse, 1988) $\mu_l = A\exp\left(\frac{B}{273.15+T}\right)\left(1+1.85\omega_l^h + 4.10\left(\omega_l^h\right)^2 + 44.5\left(\omega_l^h\right)^3\right)$

PARAMETERS FOR ICL=15, ITYCL=1

P1	ρ_{lo}	kg m^{-3}	Reference density, default=1002.6 kg.m^{-3}
P2	β	MPa^{-1}	Compressibility, default=4.5 10^{-4}
P3	α	^{o}C^{-1}	Volumetric thermal expansion coefficient for water, default=-3.4 10^{-4}
P4	γ		Solute variation, default=0.6923
P5	P_{lo}	MPa	Reference pressure, default=0.1

PARAMETERS FOR ICL=15, ITYCL=2

P1	ρ_{lo}	kg m^{-3}	Reference density, default=1002.6 kg.m^{-3}
P2	β	MPa^{-1}	Compressibility, default=4.5 10^{-4}
P3	α	^{o}C^{-1}	Volumetric thermal expansion coefficient for water, default=-3.4 10^{-4}
P4	γ		Solute variation, default=0.6923
P5	P_{lo}	MPa	Reference pressure, default=0.1

PARAMETERS FOR ICL=16, ITYCL=1

P1	A	MPa s	Pre-exponential parameter, default= 2.1 10^{-12}
P2	B	K	Exponential parameter, default=1808.5 (only used if A=B=0, but not used if A>0 and B=0)

Remark: liquid and gas density and viscosity are not material dependents. For this reason, values should be prescribed only once. If these are multiplied defined, the code will use the values it reads first.

3.10. Gas phase properties

CODES	ICL=17 and 18
DESCRIPTION	ICL=17: Dry air density. ICL=18: Gas viscosity.
EQUATIONS	ICL=17 $\rho_g = \theta_g^a + \theta_g^w$ ICL=17, ITYCL=1: law of ideal gases $\theta_g^a = \dfrac{M_a P_a}{R\left(273.15+T\right)}$ and Henry's law for dry air (as ITYCL=3 with M_a = 0.02895 and H = 10000 MPa) ICL=17, ITYCL=2: $\theta_g^a = \left(\theta_g^a\right)_o \exp(\beta(P_g - P_{go}) + \alpha T)$ Usually used to consider a second liquid phase instead of the gas phase (in that case do not consider vapour in gas phase)

	ICL=17, ITYCL=3, law of ideal gases and Henry's law for any dry gas species (as ITYCL=1, but with user defined values for gas molecular mass and Henry's constant): $\omega_l^{dgs} = \frac{P_{dgs}}{H}\frac{M_w}{M_{dgs}}$ where P_{dgs} is dry gas species pressure (air pressure in the formulation), M_w is molecular mass of water and M_{dgs} is molecular mass of dry gas species. ICL=18, ITYCL=1 (Rossel, 1974): $\mu_g = \frac{A\sqrt{273+T}}{\left(1+\frac{B}{273+T}\right)}\frac{1}{1+\frac{b_k}{P_g}}$ $b_k = C - Dk$ (k : intrinsic permeability) ICL=18, ITYCL=2: $\mu_g = A\exp\left(\frac{B}{273.15+T}\right)$

PARAMETERS FOR ICL=17, ITYCL=2

P1	$(\theta_g^a)_o$	kg m^{-3}	reference density for $T=0$ ºC
P2	β	MPa^{-1}	compressibility, default=0.0
P3	α	^{o}C^{-1}	Volumetric thermal expansion coefficient for water, default=0.0
P4			
P5	P_{lo}	MPa	reference pressure, default=0.0

PARAMETERS FOR ICL=17, ITYCL=3, (gases law with modified molecular mass and Henry's constant)

P1	M	kg mol^{-1}	molecular mass
P2	H	MPa	Henry's constant

PARAMETERS FOR ICL=18, ITYCL=1:

P1	A	MPa s	default=1.48 10^{-12}
P2	B	^{o}C	default=119.4 (only used if A=B=0, but not used if A>0 and B=0)
P3	C		default=0.14
P4	D		default=1.2 10^{15}
P5			

PARAMETERS FOR ICL=18, ITYCL=2:

P1	A	MPa s	pre-exponential parameter, default=1.48 10^{-12}
P2	B	^{o}C	exponential parameter, default=119.4 (only used if A=B=0, but not used if A>0 and B=0)
P3			

P4			
P5			

Gas phase properties can be used to consider a second liquid in the case of a two immiscible phase flow problem in a porous medium. In this case, water vapour and air dissolved must not be considered, hence, VAPOUR NOT PERMITTED and DISSOLVED AIR NOT PERMITTED should be used to avoid the species to be mixed.

3.11. Psychrometric law

CODES	None, because it requires no parameters
DESCRIPTION	Vapour density versus capillary pressure (Edlefson and Anderson, 1943; Sprackling, 1985)
EQUATIONS	$\theta_g^w = \left(\theta_g^w\right)^0 \exp\left(\frac{-\left(P_g - P_l\right)M_w}{R\left(273.15+T\right)\rho_l}\right)$ $(\theta_g^w)^0$ is the vapour density in the gaseous phase in contact with planar surface (i.e., P_l-P_g = 0). It depends on temperature and solute concentration (see chapter 3.12)

3.12. Vapour density

CODES	None, because it requires no parameters
DESCRIPTION	Law of ideal gases and vapour density with planar surface ($(\theta_g^w)^0$) versus temperature and concentration.
EQUATIONS	$\left(\theta_g^w\right)^0 = \frac{M_w P_v}{R\left(273.15+T\right)}$ $P_v = 136075 a_w \exp\left(\frac{-5239.7}{273.15+T}\right)$ MPa P_v is partial pressure of vapour and a_w is the activity of water.

If IOPTXHL=2 (card 6, chapter 4.2) a_w is calculated from the solute concentrations of the reactive transport. If IOPTXHL=0, a_w is 1.0.

3.13. Internal gas energy

CODES	None, because it requires no parameters
DESCRIPTION	Internal energy of the gas phase (E_g, J/kg)

EQUATIONS	$E_g = E_g^w \omega_g^w + E_g^a \omega_g^a$ $E_g^w = 2.5\times10^6 + 1900.0T$ $E_g^a = 1000.0T$ (Pollock, 1986)

3.14. Internal liquid energy

CODES	None, because it requires no parameters
DESCRIPTION	Internal energy of the liquid phase (E_l, J/kg)
EQUATIONS	$E_l = E_l^w \omega_l^w + E_l^a \omega_l^a + E_l^h \omega_l^h$ $\begin{cases} E_l^w = 4184.0T & \text{if IOPTXHL} = 0 \\ E_l^w = 3144.0T & \text{if IOPTXHL} \neq 0 \end{cases}$ $E_l^a = 1000.0T$ $E_l^h = 1.42\times10^5 + 2222.0T$

4. Input and Output File Description

4.1. Root input file (root.inp)

Card-1. Root
Variable: ROOT
Format: A100

ROOT: The root of most input and output files

Card-2. Options
Variable: ITRSP, IQUIM, TRSPREAC, ITASK
Format: 4I5

ITRSP: Indicates whether reactive transport has to be calculated (1) or not (0).
IQUIM: Must be equal to ITRSP
TRSPREAC: Must be equal to ITRSP
ITASK: Indicates whether only thermohydraulics (CodeBright without Retraso) has to be calculated (1) or also should include reactive transport (2). If ITRSP = 0, then ITASK must be 1; If ITRSP = 1, then ITASK must be 2

4.2. General flow input file (*root*_gen.inp)

Card 1. Problem
Variables: HEAD
Format: (A40)

Card 2. Dimensions and options
Variables: NUMNP, NUMEL, NDIM, IAXISYM, NUMMAT, NHV
Format: (10I5)

NUMNP:	Number of nodes
NUMEL:	Number of elements
NDIM:	Space dimensions (1,2,3)
IAXISYM:	Axisymmetric option: 0-no axisymmetry, 1-yes (around y-axis), NDIM=2. The principal stresses are: (σ_r (radial), σ_y (axial) σ_θ(circunferential)) NDIM=1. The principal stresses are: (σ_r(radial), σ_θ(circumferential), σ_z(axial))
NUMMAT:	Number of materials

NHV: Number of history variables (depends on the type of mechanical constitutive model used). This variable is checked internally

Card 3. Dimensions and options
Variables: NZ1, NZ2, MFRONTH, NDF, MNVAL, ISOLVE
Format: (10I5)

NZ1: =MXDIFN: maximum difference between connected nodes, this variable is read for dimensioning purposes. The node numeration of the grid is assumed to have been optimised in order to reduce the matrix band width. If θ=ε=0 are used in a non-mechanical problem, then MXDIFN can be 0 because a quasi-explicit approximation will be used, i.e. only a NDF-diagonal matrix is solved which contains derivatives of the storage terms. (See below for NZ=NZ1*NZ2).

NZ2: =MBANDT: total band width (geometrical for 1 variable), (MBANDT = 2(MXDIFN+1)-1, the user should provide a value but the code checks this value. So this entry is redundant.

NZ= NZ1*NZ2: Used only for ISOLVE=5. It is the number of nonzero-blocks in the jacobian (i.e. the number of nonzeros for NDF=1). This variable is computed as NZ=NZ1*NZ2. Since this variable is checked internally, if the number of nonzeros is not known a priori, a guess can be used and the code automatically checks its validity. Otherwise, the required value is output.

MFRONTH: void

NDF: Number of degrees of freedom per node. For instance a 2-dimension thermomechanical analysis requires NDF=3.

MNVAL: Maximum number of integration points in an element (default=1). For a two-dimensional analysis with some (not necessarily all) quadrilateral elements, MNVAL=4. For a three-dimensional analysis with some (not necessarily all) quadrilateral prism elements, MNVAL=8.

ISOLVE: solve the system of equations according to different algorithms.
ISOLVE=3: LU decomposition + backsubstitution (NAG subroutines, fonts available). (recommended option for direct solution).
ISOLVE=5: Sparse storage + CGS (conjugate gradients squared)

Card 4. Dimension boundary conditions
Variables: NFDTYPE, NFLUXTYPE
Format: (5I5)

NFDTYPE: Number of prescribed force/displacement boundary condition types. As RCB does not solve mechanical problems NFDTYPE should be 0.

NFLUXTYPE: Number of flux boundary condition types. NFLUXTYPE<=NUMNP. Boundary conditions for mass and energy balance problems are grouped in a single type due to practical reasons. See **Cards** 17 to 20 for information about the form of boundary conditions.

Boundary conditions can be applied at all nodes, even in the internal nodes.

Card 5. Options. Unknowns to be calculated.
Variables: IOPTDISPL, IOPTPL, IOPTPG, IOPTTEMP, IOPTXWS

Format: (10I5)

IOPTDISPL: =1, solving for NDIM displacements (u_x,u_y,u_z). As RCB does not solve mechanical problems IOPTDISPL should be 0.

IOPTPL: =1, solving for liquid pressure (P_l) (see IOPTPC)

IOPTPG: =1, solving for gas pressure (P_g)

IOPTTEMP: =1, solving for temperature (T)

IOPTXWS: =2, solving for a solute in liquid phase (c)

Card 6. Other options.

Variables: IOPTXHL, IUPDPOR, IOPTXWG, IOPTXAL, IOPTPC, IOPTHYS, IUPDC

Format: (10I5)

IOPTXHL: =1, halite is soluble in liquid phase. ω_l^h (the mass fraction of salt in liquid) is non-zero and considered a dependent variable on temperature. For isothermal problems this option is not very relevant because solubility has only been considered a function of temperature and not on pressure, however IOPTXHL=1 can still be used in order that the liquid phase is considered a saturated brine instead of pure water. In this case, properties of liquid phase are computed according to the concentration obtained as a function of TCONS (**Card** 8)

=2, Liquid phase properties and vapour pressures are calculated from concentrations calculated by the reactive transport module. This option requires reading more parameters for the geochemical input file (chapter 4.7, block 1 and 2).

IUPDPOR: =1, porosity is updated including not only volumetric strain, but also dissolution/precipitation (of halite, see IOPTXHL or of minerals calculated by the reactive transport module).

If IUPDPOR=0 and IOPTXHL is non zero a warning message is given because variations of porosity caused by other than deformation will be neglected. IUPDPOR=1 only makes sense for IOPTXHL=1.

IOPTXWG: =1, water vapour is NOT permitted even if the problem is non-isothermal and unsaturated. If IOPTXWG=0, water vapour is permitted and its concentration computed through psychrometric law, vapour pressure and gases law.

Using IOPTXWG = 1 (i.e. vapour concentration is not computed) is convenient when the problem is nonisothermal but the whole medium will remain saturated during the entire simulation.

IOPTXAL: =1, air dissolved is NOT permitted even if the problem is two phase (liquid and gas) flow. If IOPTXAL=0, air dissolved is permitted and its concentration computed through Henry's law.

IOPTPC: index to modify some aspects related to capillary pressure, saturation and relative permeability.

IOPTPC = 0, S_l-element is computed as a function of the capillary pressure P_g-P_l-element. (Consistent approximation, not recommended).

IOPTPC =-1, S_l -element is computed by averaging S_l -nodal values.

k_{rl}-element and k_{rg}-element are computed as a function of S_l-element (recommended option).
IOPTPC =-2, k_{rl}-element and k_{rg}-element are computed by averaging nodal values of relative permeabilites.
IOPTPC =-3, k_{rl}-element and k_{rg}-element are computed by averaging nodal values. Derivatives of relative permeabilities are also averaged.
IOPTPC =-4, k_{rl}-element and k_{rg}-element are set equal to the maximum nodal value.
IOPTPC = 1: capillary pressure is used ($P_c = P_g$-P_l) as state variable instead of P_l. If IOPTPC is = 1 then it is necessary to use IOPTXAL=1 and IOPTXWG=1, and IOPTDISPL=0 and IOPTTEMP=0. That is, IOPTPC=1 is only available for two phase immiscible fluids.

IOPTHYS: = 1: option for hysteretic behaviour of retention curve

IUPDC: = 1: updated lagrangian method, i.e., co-ordinates are modified after each time increment is solved. If deformations are very large, some elements may distort. If distortion is very large the volume of an element may become negative and the execution would terminate immediately.

Remarks: vapour and air dissolved are considered automatically depending on options in Card 5. However, if for any reason they want not to be considered, then the auxiliary indexes IOPTXWG=1 or IOPTXAL=1 can be used.

Card 7. Flags. Auxiliary options.
Variables: IFLAG1, IFLAG2, IFLAG3, IFLAG4, IGLAG5
Format: (10I5)
IFLAG1: 0
IFLAG2: 0
IFLAG3: 0
IFLAG4: 0
IFLAG5: 0
These options have been introduced for programming purposes. In general users should not use them.

Card 8. Constants.
Variables: EPSILON, THETA, PGCONS, TCONS, PLCONS
Format: (6F10.0)

EPSILON: Position of intermediate time $t^{k+\varepsilon}$ for matrix evaluation, i.e. the point where the non-linear functions are computed. (frequent values: 0.5, 1)

THETA: Position of intermediate time $t^{k+\theta}$ for vector evaluation, i.e. the point where the equation is accomplished. (frequent values: 0.5, 1)

PGCONS: Constant gas phase pressure for solving with IOPTPG=0, otherwise ignored. (frequent value: 0.1 MPa = atmospheric pressure).

TCONS: Constant temperature for solving with IOPTTEMP=0, otherwise this value is ignored.

PLCONS: Constant liquid phase pressure for solving with IOPTPL=0, otherwise ignored. (if PLCONS is greater than -1.0 x 10^{10} then wet conditions are

assumed for computing viscous coefficients in creep laws. (Otherwise the medium is considered dry.)

Card 9. Void.
This line should be left blank.

Card 10. Options.
Variables: IOWIT, INTER, ITERMAX, IOWCONTOURS, ITERMAXS, ITIME
Format: (10I5)

IOWIT: Iteration information is written in file *ROOT*_GEN.OUT according to:
IOWIT=0, no information about convergence is written. This option should be used if the user is very confident with the time discretization and not interested in details at every time step or problems with time increment reductions. Usually this happens when previous runs have shown that convergence and time discretization work very well.
IOWIT=1, partial information is written. Time intervals and time-values, number of iterations, CPU-time values, etc. are written. Convergence information is only written if time increment reductions take place.
IOWIT=2, all iteration information is written. Convergence information is written for all iterations and all time increments. This option may result in a very large file *ROOT*_GEN.OUT

INTER: Writing results frequency in *ROOT*_OUT.OUT or in *ROOT*.FLAVIA.RES. For instance, if INTER=20 results will be written only every 20 time increments, results at intermediate points will be lost, except the values at few nodes or elements that may be requested in the *ROOT*_GRI.DAT file (chapter 4.3).

ITERMAX: Maximum number of iterations per time increment

IOWCONTOURS: Option for writing results in files GID post processor.
IOWCONTOURS=0, the file *ROOT*_OUT.OUT is written.
IOWCONTOURS=2 then files for GiD are generated. These are *ROOT*.flavia.dat and *ROOT*.flavia.res.
IOWCONTOURS=4 or 5 then files for new GiD output (nodal variables at nodes, Gauss point variables at Gauss points without smoothing) are generated. These are *ROOT*.post.msh and *ROOT*.post.res. If IOWCONTOURS=4, only 1st Gauss point of each element is printed. IF IOWCONTOURS=5, all Gauss points are printed for all elements.

ITERMAXS: Maximum number of iterations for the solver, i.e. for Conjugate Gradients Squared solution (this variable is only required for ISOLVE=5).

ITIME: Time adaptation is performed as a function of several convergence criteria described in **CardGroup** 11
A new time increment is predicted from the relative error in variables of the previous time increment. If the relative error is less than *dtol=0.01*, time increment is reduced according to error deviation.
The same as 6, but with *dtol=0.001*.

CardGroup 11. Convergence parameters
Variables:

Liquid pressure:	DELMXPL, FACPL, DELQWMX, DPLMX (Omit this line if IOPTPL=0)
Gas pressure:	DELMXPG, FACPG, DELQAMX, DPGMX (Omit this line if IOPTPG=0)
Temperature:	DELMXT, FACT, DELQMX, DTMX (Omit this line if IOPTTEMP=0)
Inclusions conc.:	DELMXI, FACI, DELIMX, DIMX (Omit this line if IOPTXWS=0)

Format: (5F10.0)

Each computed unknown requires a line with its associated parameters. In this way each equation has different tolerances.

DELMXPL:	Maximum (absolute) liquid pressure error tolerance (Mpa)
FACPL:	Maximum (relative) liquid pressure error tolerance (-)
DELQWMX:	Maximum nodal water mass balance error tolerance (kg/s)
DPLMX:	Maximum liquid pressure correction per iteration (MPa) (time increment is reduced if necessary)
DELMXPG:	Maximum (absolute) gas pressure error tolerance (MPa)
FACPG:	Maximum (relative) gas pressure error tolerance (-)
DELQAMX:	Maximum nodal air mass balance error tolerance (kg/s)
DPGMX:	Maximum gas pressure correction per iteration (MPa) (time increment is reduced if necessary).
DELMXT:	Maximum (absolute) temperature error tolerance (^{o}C)
FACT:	Maximum (relative) temperature error tolerance (-)
DELEMX:	Maximum nodal energy balance error tolerance (J/s)
DTMX:	Maximum temperature correction per iteration (^{o}C) (time increment is reduced if necessary).
DELMXI:	Maximum (absolute) water in inclusion mass fraction error tolerance (-)
FACI:	Maximum (relative) water in inclusion mass fraction error tolerance (-)
DELIMX:	Maximum nodal inclusions balance error tolerance (kg/s)
DIMX:	Maximum mass fraction in solid correction per iteration (-) (time increment is reduced if necessary)

Relative error is defined as the ratio between variable correction (δx) and variable increment (Δx).

Convergence criteria are as follows (only convergence on the equation of energy balance is illustrated, but the same applies for the other equations):

If (δT < DELMXT + FACT.T) for all nodes, then convergence has been achieved (condition A). T is the value of the variable temperature.

If (q_h < DELEMX) for all nodes (q_h represents here the energy balance or residual in a node), then convergence has been achieved (condition B).

It should be mentioned that convergence in terms of δT and convergence in terms of q_h should be reached simultaneously because the Newton - Raphson is used. For this reason the program stops the iteration process and looks for another time step when one of the two conditions (A or B) is achieved. For instance if the user decides that convergence should be imposed because the residual has reached a tolerance then, DELMXT and FACT should be set to very low values.

When more than one degree of freedom is solved per node and the last option is used, convergence in terms of variable or residual should be achieved by all the variables simultaneously. In other words, it is not possible that the mechanical problem converges by residual and the thermal converges by the variable.

If (δT > DTMX), time increment will be reduced. This parameter controls the accuracy of the solution in terms of how large can be the time increments. A low value of DTMX will force to small time increments when large variations of temperature take place.

Usually, it is difficult to guess the values of the tolerances that should be used in a problem. The convergence criterion in terms of absolute terms is linked with the unknowns, and hence it also depends on the range of variation of the variable. In this case the user decides the degree of accuracy that is needed for each variable. The tolerances in relative terms are usually larger than the values for absolute.

Finally, the tolerance values for residual convergence are more difficult to guess because 'a priori' it is difficult to know the values of forces or flows equilibrating at nodes. Again the user should reach a compromise between a very strict value or a less severe condition.

Convergence parameters for Conjugate Gradients Squared method of solution (Omit this CARD if ISOLVE is not equal to 5).

Variables: DXS,DRS,DRSREL
Format: (5F10.0)
This Card is only required for ISOLVE=5.

DXS:	Maximum abs. correction for solver (usually a very low value)
DRS:	Maximum abs. residual for solver (< min(DELFMX, DELQWMX, DELQAMX, DTMX, DELIMX)) assuming all them > 0
DRSREL:	Maximum relative residual for solver. The solver residual is normalised with the RHS of the system of equations to be solved.

This group of **Card**s ends with '   -1' (forma I5).

Card 12. Gravity
Variables: GRAVITY(1), ..., GRAVITY(NDIM)
Format: (3F10.0)
GRAVITY(NDIM): gravity vector (m/s^2), usually (0,0,-9.81) for three dimensions, (0,-9.81) for two dimensions and (-9.81) for one dimension.

The following group of **Card**s, beginning with time period definition can be repeated several times to define periods or steps with different material properties and boundary

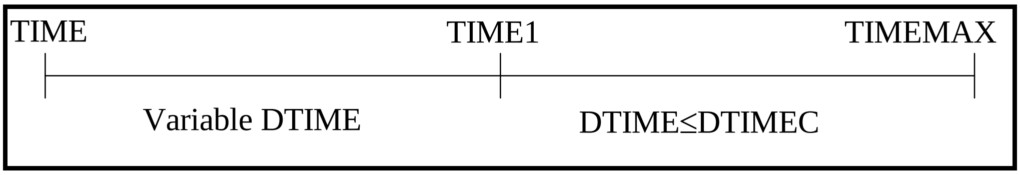
conditions. For the first step all information should be read and for the subsequent steps only modifications are required.

Card 13. Period time variables
Variables: TIMEI, DTIME, TIME1, DTIMEC, TIMEF, FACTTIME
Format: (5F10.0)

TIMEI:	Initial time. If TIMEI is not equal to final time of the last increment (TIME), then it is assumed TIMEI=TIME. Exception is made if TIMEI=0.0, in which case, 0.0 is kept as a new origin of times.
DTIME:	Initial time increment for this time interval. If DTIME=0, last DTIME value is used or, the first time increment of the calculation, a small value is considered.
TIME1:	Time from which an upper bound is prescribed for the time increment. If TIME1=0, then TIME1 is considered equal to TIMEI (the upper bound is prescribed during all the time step)
DTIMEC:	Upper bound value for the time increment used from TIME1 to TIMEMAX. If found equal to zero, no maximum time increment value is prescribed.
TIMEF:	Final time.
FACTTIME:	Factor for converting seconds (input time units) into another output time units. (Example: FACTTIME=86400. for output in days).

Time increments during time step [TIMEI1, TIMEF] are adapted by the code according to flag control ITIME (see **Card** 10). This may cause inconveniences if the user desires the results at precisely fixed times (for instance: 6 months, 1 year, 2 year, etc.). Moreover, if something changes between two runs (e.g. boundary conditions) and any time increment should be modified, the value of the times in which results are output will not be identical between the two runs. In this case, it would be difficult to make a comparison of the two analyses because we would not have the same times for output.

A first way to overcome this inconvenience is to prescribe an upper bound for the time increment, reflected in the variable DTIMEC. If convergence requires time increments smaller than DTIMEC, time increment is reduced. But, if convergence is easy and the current time increment becomes higher than DTIMEC, it is fixed to DTIMEC. Variable TIME1 allows for setting an intermediate time between TIMEI and TIMEF from which the upper bound for the increment becomes active, as represented below:



Another way to set fixed times for output results is to use a sequence of **Card**s number 13 separated by two (only flow or only mechanical problem) or three (flow and mechanical problem) lines with '-1' (format I5) indicating that nothing changes in the new time period, except the time discretization. In this way, results will be output for all

TIMEF's, and if the user is only interested in these fixed times a very large value may be used for INTER (see **Card** 10) to avoid output at other times.

Example:

-1	indicates no change in material properties				
-1	indicates no change in mechanical boundary conditions				
-1	indicates no change in flow boundary conditions				
350000.	0.0	0.0	10000.	360000.	86400.
-1	indicates no change in material properties				
-1	indicates no change in mechanical boundary conditions				
-1	indicates no change in flow boundary conditions				
360000.	0.0	0.0	10000.	370000.	86400.
-1	indicates no change in material properties				
-1	indicates no change in mechanical boundary conditions				
-1	indicates no change in flow boundary conditions				

in this case for the times 350000, 360000 and 370000 the results would be written. Time step in this case would be lesser or equal than 10000.

It is possible to define at the beginning of the calculation a step for equilibration of the initial stress state. This is done by defining a time step starting from a negative value (TIMEI <0) and ending at 0 (TIMEF = 0). During this step, gravity is applied as a ramp. Greater is time step (TIMEF – TIMEMAX), smoother is the gravity ramp.

Card 14. Number of material
Variables: IMAT
Format: (I5)
IMAT: index of material (<= NUMMAT)
(if '-1' (format I5) is read, no more materials are read, and hence, parameters will be zero (or default values when defined) or the value read in a former time period)

Card 15. Number and name of constitutive law
Variables: ICL, TIT, ITYCL
Format: (I5, A20; I5)

ICL index of constitutive law (if '-1' (format I5) is read, no more constitutive laws are read for this material). Each process considered needs one or more ICL's.

TIT text to identify (by the user) the constitutive law (ex: Retention curve), this text will be reproduced on output only for the user reference but will not be used by the program.

ITYCL type of constitutive law. For each value of ICL several relationships (different values of ITYCL) may be available.

CardGroup 16. Parameters constitutive law
Variables: TIT, PARCL(1,ICL,IMAT)=P1, TIT, PARCL(6,ICL,IMAT)=P6
TIT, PARCL(2,ICL,IMAT)=P2, TIT, PARCL(7,ICL,IMAT)=P7
TIT, PARCL(3,ICL,IMAT)=P3, TIT, PARCL(8,ICL,IMAT)=P8
TIT, PARCL(4,ICL,IMAT)=P4, TIT, PARCL(9,ICL,IMAT)=P9
TIT, PARCL(5,ICL,IMAT)=P5, TIT, PARCL(10,ICL,IMAT)=P10
Format: (A20, F10.0, A20, F10.0)
TIT: text to identify (by the user) the parameter (ex: Young

	modulus (E)), this text will be reproduced on output only for user reference but will not be used by the program
PARCL(MNP,NCL,NUMMAT):	parameters of constitutive laws (MNP=10, NCL is the maximum number of existing constitutive laws)

The matrix PARCL(MNP,NCL,NUMMAT) contains all information of parameters for the constitutive laws (for its meaning see chapter 3). A maximum of 10 parameters for each constitutive law is considered. These parameters are read in 2 columns, i.e., 5 lines are required to read each PARCL as indicated above. This is represented as:

Text Parameter 1	Value for P1	Text Parameter 6	Value for P6
Text Parameter 2	Value for P2	Text Parameter 7	Value for P7
Text Parameter 3	Value for P3	Text Parameter 8	Value for P8
Text Parameter 4	Value for P4	Text Parameter 9	Value for P9
Text Parameter 5	Value for P5	Text Parameter 10	Value for P10
A20	F10.0	A20	F10.0

Card 19. Type of Boundary Condition. Mass or heat transport problems.
Variables: IF
Format: (I5)
(Omit **Card** 19 if IOPTPL + IOPTPG + IOPTTEMP = 0)
IF: index of flux boundary condition (<= NFLUXTYPE)
(if ' -1' (format I5) is read, no more boundary condition types are expected.

CardGroup 20. Flux problem boundary condition
Variables: TIT, FLUX(1,IF), TIT, FLUX(21,IF),
TIT, FLUX(2,IF), TIT, FLUX(22,IF),
TIT, FLUX(3,IF), TIT, FLUX(23,IF),
TIT, FLUX(4,IF), TIT, FLUX(24,IF),
...
TIT, FLUX(20,IF), TIT, FLUX(40,IF),
Format: (A20, F10.0, A20, F10.0)
(Omit CardGroup 20 if IOPTPL + IOPTPG + IOPTTEMP =0)
TIT: title for each value (ex: *liquid pressure*)
FLUX(20,IF): array containing parameters for boundary conditions

TIT for FL1	Value for FL1	TIT for FL1	Value for FL1
TIT for FL2	Value for FL2	TIT for FL2	Value for FL2
...		...	
TIT for FL20	Value for FL20	TIT for FL20	Value for FL20
A20	F10.0	A20	F10.0

If FL20 equals 5.0 atmospheric boundary conditions are considered. If not, standard boundary conditions are considered. Then, the parameters are those used in equation (4), (5) and (6). There meaning is explained in the next table.

FL1	ω_g^w prescribed mass fraction (kg/kg)	FL22	
FL2	j_g prescribed gas flow rate (kg/s)	FL23	increment of j_g during time step (kg/s)
FL3	P_g prescribed gas pressure (MPa)	FL24	increment of P_g during

			time step (MPa)
FL4	γ_g (kg/s/MPa)	FL25	
FL5	β_g (kg/s/MPa)	FL26	
FL6	ρ_g prescribed gas density (kg/m^3)	FL27	
FL7	ω_l^h prescribed mass fraction of salt (kg/kg)	FL28	
FL8	ω_l^a prescribed mass fraction of air (kg/kg)	FL29	
FL9	j_l prescribed liquid flow rate (kg/s)	FL30	increment of j_l during time step (kg/s)
FL10	P_l prescribed liquid pressure (MPa)	FL31	increment of P_l during time step (MPa)
FL11	γ_l (see comments for negative value)	FL32	
FL12	β_l (kg/s/MPa)	FL33	
FL13	ρ_l prescribed liquid density (kg/m^3)	FL34	
FL14	j_e prescribed heat flow rate (J/s)	FL35	increment of j_e during time step (kg/s)
FL15	T prescribed temperature (C)	FL36	increment of T during time step (ºC)
FL16	γ_e (J/s/C)	FL37	
FL17	λ_e : positive values: [j_e=j_e*exp(-abs(λ_e)t)] is used (units 1/s). λ_e : negative values: [j_e=$j_e t^{-abs(\lambda e)}$]	FL38	
FL18	void	FL39	
FL19	δ: parameter for smoothing curve the seepage (outflow of water only) boundary condition. For a positive value a parabolic curve is used; for a negative value an exponentially decaying curve is used. δ is the distance from the reference pressure to the point of change	FL40	
FL20	*index*: auxiliary index. *index*=+1.0 means that all flow rates are nodal values *index*=-1.0 means that all flow rates are per unit volume (3-D), area(2-D) or length (1-D) of medium (internal source or sink) *index*=+2.0 means that all flow rates are per unit area (3-D) or length (2-D) (lateral fluxes). *index*=+5.0 means atmospheric boundary conditions (see below)	FL40	

A surface where seepage (only outflow for liquid phase is permitted) is possible has a boundary condition of prescribed liquid pressure. However, only liquid outflow is permitted. To recognize this fact, γ_l must be negative. This negative sign only indicates that nodes with this kind of boundary condition allow seepage.

Another situation occurs when an internal source or sink should be imposed. In this case it is preferable to use *index* = -1.0 and the program automatically considers that the nodal flows are per unit volume and will be multiplied by the volume associated to the cell centred in the node.

If there is inflow of gas or liquid phase, it is very important to give values of the following variables: ω_l^h, ω_g^w, ω_l^a, ρ_l, ρ_g and T. Otherwise they are assumed zero which is not correct because they will be far from the equilibrium. If outflow takes place, this is not relevant because the values of the medium are used.

If FL20 equals 5.0, atmospheric boundary conditions are considered as explained in chapter 2.1.4. The time varying meteorological data are given in the file *root*_atm.inp (chapter 4.4). The other parameters are entered at this cardgroup and are explained in the next table:

FL1	Latitude (rad), λ
FL2	Time when autumn starts (s), t_s
FL3	Time at noon (s) t_m
FL4	Roughness length (m), z_0
FL5	Screen height (m), z_a
FL6	Stability factor (-), ϕ
FL7	Atmospheric gas density (kg m^{-3}), ρ_{ga}
FL8	Dry albedo (-), A_d
FL9	Wet albedo (-), A_w
FL10	Liquid leakage coefficient (kg m^{-2} s^{-1} Mpa^{-1}), γ_l
FL11	Gas leakage coefficient (kg m^{-2} s^{-1} Mpa^{-1}), γ_g
FL12	Factor with which rain is multiplied (-)
FL13	Factor with which radiation is multiplied (-)
FL14	Factor with which evaporation is multiplied (-)
FL15	void
FL16	void
FL17	void
FL18	void
FL19	= 0.0: Radiation is calculated according to equations (16) to (25) = 2.0: Radiation data are read from the file *root*_atm.inp (chapter 4.4).
FL20	*index*=+5.0 means atmospheric boundary conditions

4.3. Geometrical input file (*root*_gri.inp)

The file *root*_gri.inp is read two times, for the thermohydraulic geometrical data (CodeBright) and for reactive transport geometrical data (Retraso).

Card 1. Grid writing index
Variables: IOWGRI, IOFILE, IFMT
Format: (5I5)
IOWGRI: =1, a *ROOT*MSH.DAT file is created on output

IOFILE: Way of reading geometrical input. For RCB IOFILE must be 2
IFMT: Way of reading geometrical input. For RCB IFMT must be 0.

Card 2.
Variables: FORM1
Format: (A60)
Format for reading thermohydralic element information

Card 3.
Variables: FORM2
Format: (A60)
Format for reading reactive transport element information

Cardgroup 4. Element information
Cardgroup 4 is read two times for thermhydraulic and reactive transport information.

Cardgroup 4a. Thermhydraulic element information
Variables: L, MTYPE, LTYPE, KXX(1,L), ..., KXX(MNNEL,L)
Format: FORM1

L:	element number
MTYPE(L):	material type
LTYPE(L):	element type
KXX(MNNEL,L):	global conectivities (the maximum number of connectivities is 2 (ndim=1), 6 (ndim=2), and 8 (ndim=3),

Types of elements available:

NDIM=1	LTYPE=1	Segment
NDIM=2	LTYPE=1	Linear triangle: mainly used in flow problems, i.e. when the mechanical problem is not solved. Linear triangles are not adequate for incompressible media.
	LTYPE=12	Quadratic triangle with 3 integration points. Corner nodes: 1, 2, 3; side nodes: 4, 5, 6. Integration points: 3.
	LTYPE=5	Linear quadrilateral with 4 integ. Points and selective integration by means the modification of the matrix **B** (Hughes, 1980). This allows to avoid locking when the medium is highly incompressible. (recommended quadrilateral).
	LTYPE=8	Linear segment with constant thickness. Used to simulate fractures for flow. This element does not contain mechanical properties
NDIM=3	LTYPE=1	Linear tetrahedron
	LTYPE=26	Triangular prism with 6 integr. Points
	LTYPE=3	Quadrilateral prism element with 8 integ. Points (selective integration).
	LTYPE=8	Linear segment with constant thickness. Used to simulate fractures for flow. This element does not contain mechanical properties

MNNEL is the maximum number of nodes that may have a possible element in the finite element grid that is used in a problem. With the elements that are implemented at present the following values are internally assigned to MNNEL: for NDIM=1 is MNNEL=2, for NDIM=2 is MNNEL=6, and for NDIM=3 is MNNEL=8.

Cardgroup 4b. Reactive transport element information
Variables: L, MTYPE
Format: FORM2

L:	element number
MTYPE(L):	material type

Card 5.
Variables: FORM3
Format: (A60)
Format for reading thermohydralic node information

Card 6.
Variables: FORM4
Format: (A60)
Format for reading reactive transport node information

Cardgroup 7. Node information
Cardgroup 7 is read two times for thermhydraulic (7a) and reactive transport information (7b).

Cardgroup 7a. Thermhydraulic node information
Variables: N,COORD(1,N),..., COORD(NDIM,N), IFORDISP(1,N), IFORDISP(2,N), IFORDISP(3,N), IFLUXTYPE(1,N), IFLUXTYPE(2,N), IFLUXTYPE(3,N)
Format: FORMAT3

N:	node number
COORD(NDIM,NUMNP):	nodal coordinates
IFORDISP(I,NUMNP):	integer matrix containing prescribed Force/displacement Boundary Condition code. Up to 3 force/displacement conditions can be assigned to each node. As RCB does not solve mechanical problems, dummy values can be used.
FLUXTYPE(NUMNP):	integer matrix containing prescribed Flux Boundary Condition code (0 = no boundary condition; FLUXTYPE(2,40)=8, node 40 has, as second boundary condition, the Flux Condition numbered 8 in file ROOT_GEN.DAT. Up to 3 Flux Boundary Conditions can be assigned to each node (typically used for corner nodes).

Cardgroup 7b. Reactive transport node information
Variables: N, IZONEIW(N), IZONEBW(N), IZONEM(N), IZONED(N), IZONEBG(N), IZONERW(N), IZONERG(N)
Format: FORM4

N	Node Number

IZONEIW(N)	Initial water index number specified in *root*_che.inp (chapter4.6, card 19 to 20)
IZONEBW(N)	Boundary water index number specified in *root*_che.inp (chapter4.6, card 19 to 20)
IZONEM(N)	Mineral zone index number specified in *root*_che.inp (chapter4.6, card 25 to 26)
IZONED(N)	Sorption zone index number specified in *root*_che.inp (chapter4.6, card 31 to 35)
IZONEBG(N)	Gas zone index number specified in *root*_che.inp (chapter4.6, card 39 to 41)
IZONERW(N)	Out of use (but some dummy number should be written)
IZONERG(N)	Out of use (but some dummy number should be written)

CardGroup 8. Initial values of unknowns
Variables: N, X(1,N), ..., X(NDF, N)
Format: (I5, 10F15.0)
N: Node number
X: Array containing old values of unknowns
Here, the initial values of the unknowns are read and stored as the OLD values to begin time marching calculations. In general, the following variables should be read:

n	P_l	P_g	T
I5	F15.0	F15.0	F15.0

CardGroup 9. Other element wise properties.
Variables: L, POROSITY(L), (FK(I,L),I=1,NDIM), ANISOTPER(1, L), ..., ANISOTPER(NISOT, L), THICKNESS (L), (FK(I, L), I=NDIM+1,NDIM+3)
Format: (I5, 10F15.0)

L:	element number.
POROSITY(L):	initial porosity of element L
FK(I,L):	element-wise multiplying factor for intrinsic permeability
ANISOTPER(1,L):	angle of direction of anisotropy for permeability
ANISOTPER(NISOT,L):	(NISOT =1 for NDIM=1 OR 2 ; NISOT =3 for NDIM=3)
THICKNESS (L):	(only for segment in 2-D or 3-D, LTYPE=8)
FK(I,L):	element-wise multiplying factor for retention curve parameters

Card 10. Time evolution of state or dependent variables at nodes
Variables: NOUTOT, IVOU(1), ..., IVOU(10), INTERNODE
Format: (16I5)

NOUTOT:	number of nodes for which time evolution is required
IVOU:	Variable required at these nodes. IVOU can range from 1 (first unknown) to NDF (last unknown), and from NDF+1 (first nodal dependent variable (DEPVARN vector)) to NDF+NDVN (last nodal dependent variable).
INTERNODE:	frequency for output (=1 implies all time steps).

Card 11. Nodes for time evolution
Variables: NODOUT(1), ..., NODOUT(NOUTOT)
Format: (16I5)

NODOUT(1,..,10): node number of nodes for which time evolution is required. Time evolution is written at file 'FOR050.DAT' for time steps according to INTERNODE.

Card 12. Piezometric head map
Variables: IWHEAD, NWHEAD
Format: (16I5)
IWHEAD: =1, Piezometric heads are written at file 'FOR060.DAT' or 'FOR061.DAT', depending whether liquid and/or gas phase is considered. Values for all nodes are written at times according to INTER frequence
NWHEAD: number of head contours that will be necessary in a plot. This value can be changed when drawing them

The use of this option is restricted to problems of constant density for liquid and/or gas phases.

Card 13. Nodal flows
Variables: IWNFLOW
Format: (16I5)
IWNFLOW: =1, Different flow values at boundary nodes are written at file 'FOR070.DAT'.Values are written at times according to INTER frequence. The nodal flows have units of kg/s for mass and J/s for energy
=2, the same, but values for all time steps are written
=3, the same, but values for times according to INTERNODE frequence (see **Card** 10).

Card 14. Time evolution of dependent variables at elements
Variables: LOUT, IELVOUT(1), ..., IELVOUT(10), INTERELEM
Format: (16I5)
LOUT: number of elements for which time evolution is required.
IELVOUT: Variable required at these elements. IELVOUT can range from 1 to 2 (DEPVARE vector, i.e. degree of saturation and/or porosity).
INTERELEM: frequency for output (=1 implies all time steps).

Card 15. Element numbers for time evolution of element-wise variables
Variables: NELOUT(1), ..., NELOUT(LOUT)
Format: (16I5)
NELOUT(10): Element number of elements for which time evolution is required. Time evolution is written in file 'FOR080.DAT' for time steps according to INTERELEMENT

4.4. Atmospheric data input file (*root*_atm.inp)

If atmospheric conditions are considered (FL20 = 5.0, cardgroup 20, chapter 4.2), time varying atmospheric parameters are read from this file. The theory is explained in chapter 2.1.4.

The following parameters can be read: Atmospheric temperature (^{0}C), atmospheric gas pressure (MPa), relative humidity (-), radiation (J m^{-2} s^{-1}), cloud index (-), rainfall (kg m^{-2} s^{-1}) and wind velocity (m s^{-1}). One can use two options: interpolation and simulation. Interpolation uses a simple linear interpolation of the specified parameters versus time. Simulation uses the following sinusoidal expression:

$$a = m + a_a \sin\left(2\pi \frac{t - t_a}{d_a}\right) + a_d \sin\left(2\pi \frac{t - t_d}{d_d}\right)$$

where a is the value of the parameter, m is its mean value, a_a is its annual amplitude, a_d its daily amplitude, t_a is the start of the annual variation, t_d is the start of the daily variation, d_a is the duration of a year (= 365.241 days = 3.15568×10^7 s) and d_a is the duration of a day (= 86400 s).

The file is read with free format and has the following structure. Every parameter has two columns

Column 1-2	Atmospheric temperature, T_a (^{0}C)
Column 3-4	Atmospheric gas pressure, P_{ga} (MPa)
Column 5-6	Relative humidity, H_r (-)
Column 7-8	Radiation, R_n (J m^{-2} s^{-1}) only used if FL19 = 3.0 (cardgroup 20, chapter 4.2)
Column 9-10	Cloud index, I_n (-); I_n = 1 for a clear sky; I_n = 0 for a completely cloudy sky
Column 11-12	Rainfall, P (kg m^{-2} s^{-1})
Column 13-14	Wind velocity, v_a (m s^{-1}).

The first line of the file contains the number of lines (excluding this one) and number of columns that has to be read. The second line refers to interpolation or simulation option. The following seven lines refer to the simulation parameters and all other lines to the parameters to be interpolated:

Atmospheric temperature		Atmospheric gas pressure		....
0: simulation 1: interpolation	Not used	0: simulation 1: interpolation	Not used	....
Not used	m	Not used	m	....
Not used	a_a	Not used	a_a	....
Not used	t_a	Not used	t_a	....
Not used	a_d	Not used	a_d	....
Not used	t_d	Not used	t_d	....
Not used	Not used	Not used	No se usa	....
Time 1	Temperature 1	Time 1	Pressure 1	....

Time 2	Temperature 2	Time 2	Pressure 2	....
:	:	:	:	

4.5. Transport input file (*root*_trn.inp)

In the input file for transport parameters three types of lines are distinguished:

Title section lines starting with '*', e.g.:

```
*TIME INCREMENTS
```

Comment lines starting with '!', e.g.:

```
! This is a comment
```

Value lines starting neither with '*' neither with '!', e.g.:

```
TOLAD = 1.0d-4
1     0.0    0.00     0.0      1.0  0.9D-1  0.9D-2
```

The last type is divided into two subtypes:
Scalar values characterized by the name of the variable followed by a '=' and the value of the variable, e.g.:

```
TOLAD = 1.0d-4
```

Vector values with fixed format and whose meaning depends on the section where it is found, e.g.:

```
1     0.0    0.00     0.0      1.0  0.9D-1  0.9D-2
```

The vector values have to follow immediately the corresponding section title. No blank lines or comments are permitted. E.g., the following is permitted:

```
*TIME INCREMENTS
1     5.0e2  500   1.0e+00       1.0       1.0
```

But the following is not permitted:

```
*TIME INCREMENTS
! Comment
1     5.0e2  500   1.0e+00       1.0       1.0
```

neither:

```
*TIME INCREMENTS

1     5.0e2  500   1.0e+00       1.0       1.0
! Comment
```

The only exception to the previous rule are the sections '*OPTIONS', '*PARAMETERS', '*DIMENSIONS' and '*END DATA', because their contents are only scalar variables.

Except for the lines for vector values, everything written after a '!' is considered a comment, e.g.:

```
IOPFLU = 1 ! Transient flow
```

or:

```
*TIMEINCREMENTS !__I TIMEINT NSTEP DTMIN FACDTI FACDTR
```

Almost all scalar values have a default value. If the desired value equals the default value, its corresponding line can be omitted.

Sections are identified by their first six characters (asterisk + 5). The names of the scalar variables are identified by their first eight characters

In what follows, the sections and their contents are described.

***OPTIONS**

This section contains the following scalar values:

TITLE	Title of the problem (a text)
IOPFLU	Indicates whether flow is steady state (0) or transient (1). For steady state the program calculates flow for the first time step and assumes steady state is reached for that time step. Default: 0.
IOPGASTR	Indicates whether gaseous species are transported by advection, diffusion and dispersion (1) or not (0). Default: 0.
IOPSI	Indicates whether units are in the International System (1) or not (0). Default: 1 (actually, the program is not tested well for IOPSI=0).
IOPDIFMOL	Indicates whether the gas molecular diffusion coefficient is to be a function of the temperature and pressure (1) or not (0). It is advised to use a value of 1 although the default value is 0.
IOPTORL	Option for the calculation of the tortuosity (τ) of the liquid diffusion: 0: $\tau = 1$; 1: $\tau = \sqrt{(\phi S_g)}$; 2: $\tau = (\phi S_g)^{7/3}/(\phi)^2$. Default: 0.
IOPTORG	Option for the calculation of the tortuosity (τ) of the gas diffusion: 0: $\tau = 1$; 1: $\tau = \sqrt{(\phi S_l)}$; 2: $\tau = (\phi S_l)^{7/3}/(\phi)^2$, see equations (115) and (116), chapter 2.3.1. Default: 0.
IOPDIFANI	Indicates whether the molecular diffusion is isotropic (0) or anisotropic (1). Default: 0.
IOPSATINNODES	Obsolete option. One should always use iopsatinnodes = 1, although default is 0.
ISWITCH	Indicates whether the set of primary and secondary species is changed automatically (1) or not (0). Default: 1.
NJACOB	The frequency with which the jacobain matrix is updated. Default: 1.
IOPBGPUNITS	Indicates whether the gas concentrations at the boundaries are expressed in molar fraction (1) or in partial pressure (0). Default: 0.
IOPGASSOURCE	Indicates whether chemical changes of the gas phase should be included as source/sink terms for the flow problem (1) or not (0). Option 1 does not work, so always use 0, although default is 1.
IOPCSCP	Indicates whether the concentrations of secondary species are to be calculated by a Picard approach (0) or a Newton-Raphson approach (1). Default: 0.
ISOLVETR	Indicates the type of linear solver for the transport system. 0: LU

decomposition of a banded matrix, 1: LU decomposition of a sparse matrix (according to Harwell library). Default: 0.

***PARAMETERS**

This section contains the following scalar values:

THETATRA	Time weighting factor for the transport equation. Default: 1.0
TOLTR	Absolute mass balance error tolerance convergence criterion. Default: 10^{-4}
MAXITPCH	Maximum number of Newton-Raphson iterations. Default: 100
TOLCH	Relative concentration error tolerance convergence criterion. Default: 10^{-4}
MAXITPAD	Maximum number of Newton-Raphson iterations for calculations of adsorption. Default: 100
TOLAD	Relative concentration error tolerance convergence criterion for calculations of adsorption. Default: 10^{-4}
MAXDIVERG	Maximum number of diverging Newton-Raphson iterations. Default: 3
FAC_UPD	Maximum factor for updating concentrations after a Newton-Raphson iteration. Default: 10.0

***DIMENSIONS**

This section contains the following scalar values:

NTIMINT	Number of periods with different time steps (controls the number of lines at *TIMEINCREMENTS. Default: 0 (gives error).
NWXY	Frequency of time steps that writes results versus space. Default: 1.
NWDIM	Obsolete. NWDIM should always be 2, although default value is 1.
NWTI	Frequency of time steps, that writes reactive transport results versus time for certain nodes (specified at *W_NODES). Default: 1.
NWNOD	Number of nodes (specified at *W_NODES) for writing reactive transport results versus time. Default: 0.
NWCOM	Number of components (specified in *W_COMPONENTS) of which the total aqueous concentration is written. Default: 0.
NWMIN	Number of minerals (specified in *W_MINERALS) of which the concentration and saturation index is written. Default: 0.
NWCNC	Number of aqueous species (specified in *W_CONCENTRATIONS) of which the concentration is written. Default: 0.
NWGAS	Number of gaseous species (specified in *W_CONCENTRATIONS) of which the partial pressure is written. Default: 0.

***TIMEINCREMENTS**

This section should contain NTIMINT lines with format (I5,F10.3,I5,4F10.3), one for each period.

I	Number of the period
TIMEINT	Duration of the period (in seconds)
NSTEP	Minimum number of time steps of the period (an automatic time step control can increase this number).
DTMIN	Minimum time step. The program stops if the automatic time step control

calculates a time step < DTMIN

FACDTI Time step increase factor, when Newton-Raphson converges well, that is, with a number of iterations < 0.1×MAXITPCH.

FACDTR Time step decrease factor, when Newton-Raphson converges badly, that is, with a number of iteration > 0.7×MAXITPCH, diverges more than MAXDIVERG times or anomalous concentrations are calculated.

At least there have to be one period, that is, NTIMINT ≥ 1.

***MATERIAL_PROPERTIES**

This section should contain NUMMAT (see Card 2 of *root*_gen.inp, chapter 4.2, and the materials of the elements in *root*_gri.inp, chapter 4.3) lines with format (I5,6F8.0), one for each material.

I Number of the material
DFM Liquid molecular diffusion coefficient ($m^2\ s^{-1}$)
DSL Liquid longitudinal dispersion coefficient (m)
DST Liquid transversal dispersion coefficient (m)
DFMg Factor with which the gas molecular diffusion coefficient is multiplied. The gas molecular diffusion coefficient is calculated internally by the program as a function of temperature, pressure and gaseous species.
DSLg Gas longitudinal dispersion coefficient (m)
DSTg Gas transversal dispersion coefficient (m)

If the diffusion is anisotropic (IOPDIFANI = 1), DFM and DFMg are repeated NDIM (card 2 of file *root*_gen.inp, chapter 4.2) times, being the diffusion coefficient in every direction of NDIM.

At least there must be one line. The variables DFMg, DSLg and DSTg are not used when there are no gaseous species or when they are not transported (IOPGASTR = 0).

***W_NODES**

Nodes for which reactive transport results are written versus time. Its format is (<NWNODES>I5). If NWNODES equals 0, this section should be omitted.

***W_COMPENENTS**

Numbers of the components for which the total aqueous concentration has to be written. The numbers refer to the primary species specified in the file *root*_che.inp (chapter 4.6). Its format is (<NWCOM>I5). If NWCOM equals 0, this section should be omitted.

***W_MINERALS**

Numbers of the minerals for which concentration and saturation index have to be written. The numbers refer to the minerals specified in the file *root*_che.inp (chapter 4.6). Its format is (<NWMIN>I5). If NWMIN equals 0, this section should be omitted.

***W_CONCENTRATIONS**

Numbers of the aqueous species for which the concentration has to be written. The numbers refer to the primary and secondary species specified in the file *root*_che.inp (chapter 4.6). Its format is (<NWCNC>I5). If NWCNC equals 0, this section should be omitted.

***W_GASES**

Numbers of the gaseous species for which the partial pressure has to be written. The numbers refer to the gaseous species specified in the file *root*_che.inp (chapter 4.6). Its format is (<NWGAS>I5). If NWGAS equals 0, this section should be omitted.

***LIQ_BOUNDARYCONDITIONS**

This section should contain as many lines as total number of liquid boundary conditions indicated in the file *root*_gri.inp (second column of node properties, chapter 4.3), one for each liquid boundary condition zone. Its format is (3I5,F10.0). The theory is explained in chapter 2.3.2.

I	Zone number (corresponding to that specified in the file *root*_gri.inp)
IDBOC	Type of boundary condition: 0 natural; 1: Fixed concentration (specified in the file *root*_che.inp); 2 Fixed mass flux equal to liquid flux times concentration (specified in the file *root*_che.inp); 3 Fixed mass flux (specified in the file *root*_che.inp); 4 Mixed condition
IZONEBW	Number of the chemical boundary zone specified in the file *root*_che.inp (chapter 4.6). If omitted or given a value of 0, IZONEBW is supposed to be equal to I.
GAMMAW	Coefficient for the mixed boundary condition (only necessary if IDBOC = 4)

***GAS_BOUNDARYCONDITIONS**

This section should contain as many lines as total number of gas boundary conditions indicated in the file *root*_gri.inp (fifth column of node properties, chapter 4.6), one for each gas boundary condition zone. Its format is (3I5,F10.0). The theory is explained in chapter 2.3.2.

I	Zone number (corresponding to that specified in the file *root*_gri.inp)
IDBOC	Type of boundary condition: 0 natural; 1: Fixed concentration (specified in the file *root*_che.inp); 2 Fixed mass flux equal to gas flux times concentration (specified in the file *root*_che.inp); 3 Fixed mass flux (specified in the file *root*_che.inp); 4 Mixed condition
IZONEBG	Number of the chemical boundary zone specified in the file *root*_che.inp (see chapter 4.6). If omitted or given a value of 0, IZONEBW is supposed to be equal to I.
GAMMAG	Coefficient for the mixed boundary condition (only necessary if IDBOC = 4)

***END_DATA**

Indicates the end of the data input. Lines following this section are not read.

4.6. Geochemical input file (*root*_che.inp)

The aim of this part is to define all the species that will be used in the problem: aqueous species, minerals, gases, exchanged and surface-sorbed species.

The method for specifying the primary and secondary species is based on that devised by Peter Lichtner for the code MPATH and used by Carl Steefel for the code 1DREACT (Steefel, 1993). The code RCB requires the user to specify a set of aqueous primary species (or component species) to determine the number of independent components of the system. The choice of aqueous primary species is not unique, and the set of most abundant species for each component is recommended to avoid numerical problems. The set of primary species do not need to coincide with those of defined in the thermodynamic databases master25 or mastertemp. The routine database is able to express the secondary species (aqueous complexes, minerals, gases, surface complexes) as a function of the set of primary species defined in the chemical system. Unlike conventional geochemical modelling codes, the user can select the secondary species selected that will be involved in the calculations. This allows to perform chemically simplified calculations very useful for multicomponent reactive transport problems. The amount of computing time saved is significant compared with the codes assembling a conventional transport and geochemical codes.

Firstly, the user must be sure that the set of secondary species describe the problem. The run of a geochemical speciation code, such as PHREEQC or EQ3NR, for the different expected situations of the problem is recommended in preparing the definition of the chemical input for a reactive transport problem.

Secondly, the user must include among the primary or secondary species the species used in describing the reaction in the masster25 or mastertemp database. If this is not done, the code will not be able to find the reaction in the database. For example, Al^{3+} must appear among the aqueous species, either primary of secondary, if aluminum is included in the calculations.

Redox reactions require the species O_2(aq) to be included either as a primary species or as a aqueous complex. However, since O_2(g) is the basis species for redox reactions in the database, O_2(g) must be also included in the list of gases if redox reactions are to be considered. If redox calculations are preferred as a function of 'e-', this species must be included as a primary species, then O_2(aq) must be included in the aqueous complex set, and O_2(g) in the list of gases.

RCB can consider several sorption models and empirical relationships at the same time, although several sorprios sites for the same model aren ot allowed. For each model, the user has to introduce the name of the model selected, the name of the species representing the empty sorption sites (XOH in thermodynamic models, X in empirical relationships and exchange), and the name of all the sorbed species involved.

The system may be divided into zones with different initial porous solutions. Also solutions with differentiated chemical composition may flow trough the boundaries and as recharge (infiltration, injection wells, etc.). The system may also be divided in

lithological zones with different mineral constituents, surface sorption or cationic exchange properties.

For each type of solution, RCB calculates the concentration of the primary and secondary aqueous species from given constraints: total solute concentration, fixed activity of a species, electric neutrality, and equilibrium with a mineral or with a given partial pressure of a gas. Unlike conventional geochemical speciation codes, RCB does not contain pre-optimization routines. Therefore, a stop of the calculations often occurs due to an inadequate first guess of the concentration of the aqueous primary species. The use of an independent geochemical speciation code in the preparation of the guessed values may save several trials with RCB.

The mineral proportions and the total sorption capacity of each zone of the rock system are introduced directly and no additional information is required.

The initialization of the chemical characteristics of the system is stablished by direct assigning an initial water type, mineral zone, cationic exchange zone and surface sorption zone to each node of the numerical grid. The assigning is done within the transport data input. The initial nodal temperature is checked against the temperature of the water type speciation. The concentration of sorbed species is calculated for each node from the concentration of aqueous species and the sorption characteristics of the rock.

Only the concentration of the mobile species (in aqueous and gas phase) is considered for establishing the boundary conditions. Similarly to the initial conditions, the chemical characteristics of the boundary waters is established by assigning of a chemical water type to each boundary or recharge flow in the transport input data. The chemical characteristics of the boundary gases are established by the partial pressure of all gases (see chapter 2.3.2).

Card-1. Title
Variable: TITLE
Format: A76 (write TITLE within 'single quotes')

Card-2. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')
    LABEL: comments which will appear in the output file

The cards 3 to 15 contain the information on the aqueous species, minerals, gases, surface complexes and exchangeable cations involved in the system. The names of the aqueous species, minerals and gases should be written according to those labelled in master25.dat and mastertemp.dat database (chapter 4.7).

Card-3. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')
    LABEL: comments which will appear in the output file

Card-4. Initial temperature
Variable: TC2, IACT
Format: F10.0,I5

TC2: Temperature (°C) of reference to define de system

IACT: 0: The Debye Hückel formula is used for calculation of the activity of aqueous species; 1: The Truesdell-Jones formula is used. The last option requires reading more parameters for the geochemical input file (chapter 4.7, block 1 and 2).

Card-5. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')

LABEL: comments which will appear in the output file

Card-6. Primary aqueous species
Repeat Card-6 as many times as needed
Variable: NAPRI(k)
Format: A20 (write NAPRI within 'single quotes')

NAPRI(k): Name of the kth primary species considered as primary species or base species to describe the reactions with the rest of species, minerals or gases. The species '*' is needed to indicate the end of the list.

Card-7. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')

LABEL: comments which will appear in the output file

Card-8. Aqueous complexes
Repeat Card-8 as many times as needed
Variable: NAAQX(k)
Format: A20 (write NAAQX within 'single quotes')

NAAQX(k): Name of the kth aqueous complex. Omit naaqx if no aqueous complexes are required. However, the species '*' is always needed to indicate the end of the list.

Card-9. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')

LABEL: comments which will appear in the output file

Card-10. Mineral names
Repeat Card-10 as many times as needed
Variable: NAMIN(k) IMEQ(k)
Format: A20 (write NAMIN within 'single quotes')

NAMIN(k): Name of the kth mineral phase. Omit namin if no minerals are required. However, the species '*' is always needed to indicate the end of the list.

IMEQ(k): Flag indicating the dissolution/precipitation model: 0: equilibrium mineral-solution. 1: kinetic law for precipitation-dissolution of eqn. (94), expressed in mol per volume of rock. 2: kinetic law or precipitation-dissolution of

eqn. (94), expressed in mol per mass of water. 3: Monod kinetic law of eqn. (95), expressed in mol per mass of water.
For imeq equal to 1, 2 or 3, rate law parameters must be defined in the datafile ‘kinetics.dat’ (see chapter 4.8).

Card-11. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')
LABEL: comments which will appear in the output file

Card-12. Gases
Repeat Card-12 as many times as needed
Variable: NAGAS(k)
Format: A20 (write NAGAS within 'single quotes')
NAGAS(k): Name of the kth gas. If gaseous species are transported (IOPGASTR=1, see chapter 4.5), the last species refer to the majority species of the gas phase required for the calculation of diffusion coefficients according to equation (117). If redox reactions are present in the system the species 'o2(g)' must be included as a gas species. Omit nagas if no gases are required. However, the species '*' is always needed to indicate the end of the list.

Card-13. LABEL
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')
LABEL: comments which will appear in the output file

Repeat card 14 and 15 as many times as needed up to 5 sorption models.

Card-14. Adsorption model
Variable: ADSMOD
Format: A2 (write ADSMOD within 'single quotes')
ADSMOD meaning:TL= Triple Layer Model; DL= Double Layer Model; CC= Constant Capacity Model; EQ= non-electrostatic equilibrium model; LA= Langmuir Adsorption; FR= Freundlich Adsorption; KD= Partition coefficient; EX= Cation Exchange

Card-15. Surface complexes
Repeat Card-15 as many times as needed
Variable: NAADS(k)
Format: A20 (write NAADS within 'single quotes')
NAADS(k): Name of the kth surface complex. The first name, NAADS(1), accounts for the species describing the empty sorption sites (XOH, X1OH, X2OH, X, X1, X2, etc.). Only the last name of the sorption model must be '*'. Omit ADSMOD and NAADS if no surface complexes are required. However, the species '*' is always needed to indicate the end of the list.

Card-16. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')

LABEL: comments which will appear in the output file

Card 17. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')
LABEL: comments which will appear in the output file

Card-18. Data related with the number of aqueous solutions
Variable: NITYPE NBTYPE NRWTYPE
Format: I4 I4 I4
NITYPE: Number of different aqueous solutions initially present in the system
NBTYPE: Number of different boundary solutions
NRWTYPE: Number of different recharge solutions

Cards 19 to 21 describe the different aqueous solutions (initial porous water, lateral and vertical recharges flowing into the aquifer). Repeat the following Cards 19, 20 and 21 a number of times equal to (niwtype +nbwtype +nrwtype), starting with initial concentrations, then boundary and finally recharge concentrations.

Card-19. Identification of the solution
Variable: IWTYPE TC2
Format: I4 Free
IWTYPE: Number of order of the initial, boundary or recharge solution. The value of iwtype varies from 1 to niwtype, then starts again with 1 up to nbwtype, and finally starts again from 1 up to nrwtype.
TC2: Temperature of the solution (°C)

Card-20. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')
LABEL: comments which will appear in the output file

Card-21. Data related to the chemical definition of the solution
Variable: NAPRI(k) ICON(k) CGUESS(k) CTOT(k) NADUM(k)
Format A20 I4 Free Free A20
NAPRI(k): Name of the kth primary aqueous species. The name of the species should coincide with those previously listed as primary species in the definition of the system, although the order may change. Names must be included between 'single quotes'. The species '*' indicates the end of the list of species
ICON(k): Flag indicating the type of constrain controlling the solute content which is given under ctot: 1=the concentration of the kth species is constrained by the total concentration of solute ctot, except for water which is assumed unity. 2= the concentration of the kth species calculated through charge balance. 3= the activity of the kth species is assumed initially equal to ctot. 4=the concentration of the kth species is calculated from the equilibrium of the solution with the mineral nadum(k). 5=the concentration of the kth species is calculated from the equilibrium with a partial pressure of the gas nadum(k).
CGUESS(k): Initial guess for the concentration (mol/kg) of the kth species

CTOT(k): Total solute concentration (mol/kg). In case of icon=5, ctot is the partial pressure of the gas used to constrain the concentration of the species.
NADUM(k): Name of the mineral (icon(k)=4) or gas (icon(k)=5) used to constrain the concentration of the species. Names must be included between 'single quotes'. The name of the constraint should coincide with one of those previously listed as minerals or gases in the definition of the system.

Cards 22 to 24 describe the different mineral zones initially forming the system

Card-22. Label
Variable: LABEL
Format: A76 (write LABEL within ‘single quotes’)
LABEL: comments which will appear in the output file

Card-23. Label
Variable: LABEL
Format: A76 (write LABEL within ‘single quotes’)
LABEL: comments which will appear in the output file

Card-24.
Variable: NMTYPE
Format: I4
NMTYPE: Number of mineral zones forming the system.

The following cards 25, 26 and 27 must be repeated nmtype times.

Card-25.
Variable: IMTYPE
Format: I4
IMTYPE: Number of order of the mineral zone

Card-26. Label
Variable: LABEL
Format: A76 (write LABEL within ‘single quotes’)
LABEL: comments which will appear in the output file

Card-27. Data related to the composition of the mineral zone
Variable: NAMIN(k) VF(k) AREAM(k)
Format: A20 Free Free
NAMIN(k): Name of the kth mineral involved in the lithology. The name of the mineral must be included among those previously listed in the definition of the system, although the order may change, and it is not needed to repeat the complete list. Names must be included between 'single quotes'. The mineral '*' indicates the end of the list of species.
VF(k): Volume fraction of the kth mineral. The values varies (between 0.0 and 1.0).
AREAM(k): Initial reactive surface area of the kth mineral (m^2 min/ m^3 rock)

Cards 28 to 30 describe the characteristics of the zones with different surface adsorption properties present in the system.

Card-28. Label
Variable: LABEL
Format: A76 (write LABEL within ‘single quotes’)
LABEL: comments which will appear in the output file

Card-29. Label
Variable: LABEL
Format: A76 (write LABEL within ‘single quotes’)
LABEL: comments which will appear in the output file

Card-30.
Variable: NDTYPE
Format: I4
NDTYPE: Number of surface adsorption zones

The following cards 31 to 35 must be repeated ndtype times.

Card-31.
Variable: IDTYPE
Format: I4
IMTYPE: Number of order of the adsorption zone

The following cards 32 to 35 must be repeated for each sorption model previously defined by the repetition of cards 14 and 15.

Card-32. Capacitance
Variable: LABEL C1
Format: A30 Free
LABEL: comments which will appear in the output file
C1: Capacitance (in F/m2) of the internal layer in the Triple Layer Model. Capacitance (in F/m2) in the Double Layer and Constant Capacity Models

Card-33. Capacitance
Variable: LABEL C2
Format: A30 Free
LABEL: comments which will appear in the output file
C1: Capacitance (in F/m2) of the external layer in the Triple Layer Model. Disconnected in the rest of models

Card-34. Sorbing surface
Variable: LABEL SUPADS
Format: A30 Free
LABEL: comments which will appear in the output file
SUPADS: Specific sorbing surface of the solid (in m2/ l solution)

Card-35. Sorption sites

Variable: LABEL TSS
Format: A30 Free

LABEL: comments which will appear in the output file
TSS: Total sorption sites (in mol/ l solution) of the solid surface. Exchange capacity (in eq/ l solution) in the case of cation EXchange model

Cards 36 and 37 allow the user to be sure that the chemical data have been entirely read.

Card-36. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')

LABEL: comments which will appear in the output file

Card-37. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')

LABEL: comments which will appear in the output file

Card-38.
Variable: NGTYPE
Format: I4

NGTYPE: Number of surface gas boundary zones

The following cards 39 to 41 must be repeated ngtype times.

Card-39.
Variable: IGTYPE
Format: I4

IGTYPE: Number of order of the gas boundary zone

Card-40. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')

LABEL: comments which will appear in the output file

Card-41. Data related to the composition of the gas boundary zone
Variable: NAGAS(k) PG(k)
Format: A20 Free

NAGAS(k): Name of the kth gas involved. The name of the gas must be included among those previously listed in the definition of the system, although the order may change. Names must be included between 'single quotes'. The gas '*' indicates the end of the list of species.
PG(k): Partial pressure (if IOPBGPUNITS = 0, see chapter 4.5) or molar fraction (if IOPBGPUNITS = 1) of the gas.

Card-42. Label
Variable: LABEL
Format: A76 (write LABEL within 'single quotes')

LABEL: comments which will appear in the output file

Card-43. Label to check the end of chemical data input
Variable: LABEL
Format: A76 (write LABEL within ‘single quotes’)
LABEL: This label must be ‘end’.

4.7. Geochemical database file (master25.dat or mastertemp.dat)

Two versions of a thermodynamic database are attached to RCB: master25.dat and mastertemp.dat. Master25.dat is only valid for 25°C and 1 bar, and mastertemp is an extension from 0 to 300°C and pressure along the steam saturation curve. Mastertemp is automatically activated when an input temperature is different from 25°C. Both files of database are modified versions of the EQ3/6 database created by Peter Lichtner for the code MPATH. An extension for surface complexation reactions has been incorporated in RCB. New species and reactions are easily added to the database, and the existing data are modified according to the following description.

Both databases, master25.dat and mastertemp.dat, are divided into a first line and five blocks of data. The two databases have the same internal structure, and the following description is equally valid for both of them. The first line of the database contains the total number of log K entries and the temperatures of each log K entry. The first block is a list of species which will initially be used in EQ3/6 database as component species to build the rest of reactions in the database. They do not necessarily need to be primary species in RCB (see chapter 4.6). The second block contains data concerning the rest of aqueous species or aqueous complexes, the third block mineral data, the fourth block data for gases and the fifth block data for surface complexes. The different blocks are separated by a line beginning with the string 'null'.

First line
It includes 'temperature points' N T_1 T_2 ... T_N, separated by blank spaces, where N is the number of temperature data, and T are the temperatures (in °C) of the log K values of the reactions in the database. In master25.dat file N is 1, and T_1 is 25°C.

Block 1: component species
Each line includes the 'species name' (in single quotes), the ion size, the charge of the component species, the Truesdell-Jones b parameter and the molecular weight (in kg mol^{-1}), separated by blank spaces. If the extended Debye-Hückel approach (bdot) is used for the calculation of the activity instead of Truesdell-Jones (IACT = 0, card 4 of *root*_che.inp, chapter 4.6) and if influences of the concentration on the flow are neglected (IOPTXHL=0, card 6 of *root*_gen.inp, chapter 4.2) the Truesdell-Jones b parameter and the molecular weight are not read. If the Truesdell-Jones parameter of the species is negative, the extended Debye-Hückel formula will be used for this species, also when IACT = 1.

Block 2: aqueous complexes

Each line includes the 'species name' (in single quotes) of the aqueous complex, the number of component species involved in the dissociation reaction, the stoichiometric coefficient and the 'name of comp. species' (in single quotes), N-values of logK (N defined in the first line), the ion size, the charge, the Truesdell-Jones bdot parameter and the molecular weight (in kg mol^{-1}) of the aqueous complex, and a final optional 'comment' (in single quotes). If the extended Debye-Hückel approach (bdot) is used for the calculation of the activity instead of Truesdell-Jones (IACT = 0, card 4 of *root*_che.inp, chapter 4.6) and if influences of the concentration on the flow are neglected (IOPTXHL=0, card 6 of *root*_gen.inp, chapter 4.2) the Truesdell-Jones bdot parameter and the molecular weight are not read. If the Truesdell-Jones parameter of the species is negative, the extended Debye-Hückel formula will be used for this species, also when IACT = 1.

Block 3: minerals
Each line includes the 'mineral name', the molar volume (in cm^3mol^{-1}), the number of comp. species involved in the dissolution reaction, the stoichiometric coefficient and the 'name of comp. species' (in single quotes), N-values of logK (N defined in the first line), and a final optional 'comment' (in single quotes).

Block 4: gases
Each line includes the 'gas name', the molecular weight (in g mol^{-1}), the diffusion volume of equation (117), the number of comp. species involved in the gas dissolution reaction, the stoichiometric coefficient and the 'name of comp. species' (in single quotes), N-values of logK (N defined in the first line), and a final optional 'comment' (in single quotes).

Block 5: surface complexes
Each line includes the 'surface-complex name', the number of comp. species involved in the reaction, the stoichiometric coefficient and the 'name of comp. species' involved in the desorption reaction (in single quotes), the N-values of logK (N defined in the first line) and the charge of the surface complex, and a final optional 'comment' (in single quotes). In the case of sorption empirical relationships, the log K value of the database is the log10 of the experimentl partition coefficient, and the charge value is replaced by the exponent of the Freundlich equation. In the case of cation exchange, the log K value is the log10 of the exchange coefficient of the half-reaction, which is equivalent to the log10 of the experimental exchange coefficent with respect to Na. Note that log K for X-Na species should be 0.

The reactions of the database are written with the aqueous complex, mineral, gas or surface complex on the left hand side, and the component species in the right hand side. Therefore, the log K sign corresponds to the reaction of consumption of one mole of aqueous complex, mineral, gas or surface complex.

In the case of mastertemp, when a log K entry is unknown is represented with the value 500.00. In the case of redox species 'o2(g)' is required as a component species in the description of the reaction.

4.8. Kinetic database file (kinetics.dat)

A database containing the data to describe the kinetic rate law for dissolution/precipitation of minerals is attached to RCB: kinetics.dat. Each mineral data are written in two or more lines.

If imeq (see chapter 4.6, card 10) equals 1 or 2, they have the following meaning:

The first line contains:
number of terms of the polynomial expression (N_k in Eqn, (94))
activation energy (kcal mol^{-1})
supersaturation threshold for precipitation to start
comments

N_K lines follow. Each line corresponds to one term of the polynomial law, and contains:
kinetic rate constant (k in Eqn. (94))
order of the saturation (θ in Eqn. (94))
order of the far-from-equilibrium term (η in Eqn. (94))
number of catalyzers
name of the catalyzer aqueous species
order of the activity of the catalyzer (p in Eqn. (94))

To omit the far from equilibrium term the option η = 0, since θ = 0 may cause numerical problems.

If imeq (see chapter 4.6, card 10) equals 3, they have the following meaning:

The first line contains:
number of terms of the polynomial expression (N_k in Eqn (95))
dummy parameter
dummy parameter
comments

N_K lines follow. Each line corresponds to one term of the polynomial law, and contains:
kinetic rate constant (k in Eqn.(96), (97) or (98))
indicator whether the term is p-order (1), monod (2) or monod inhibition (3)
dummy parameter
number of catalyzers (N_s in Eqn. (96), (97) or (98))
name of the catalyzer aqueous species
order of the activity of the catalyzer (p in Eqn.(96), (97) or (98))

4.9. Output files

A list of all possible output files in alphabetic order is given below. Most reactive transport results can be given versus time (for some specified nodes) and versus space

(for all nodes). The frequency of the results versus time and versus space is controlled by, respectively, NWTI and NWXY of the file *root*_trn.inp (chapter 4.5). The nodes for results versus time are controlled by NWNODES and *W_NODES of the same file.

fort.<50+*n*-1>	Node thermohydraulic properties versus time, where *n* is IVOU (see card 7 and 8 of the file *root*_gri.inp, chapter 4.3).
fort.70	Nodal flows versus time (see card 10 of the file *root*_gri.inp, chapter 4.3).
fort.<80+*n*-1>	Element thermohydraulic properties versus time, where *n* is IELVOUT (see card 11 and 12 of the file *root*_gri.inp, chapter 4.3).
fort.<200+*n*>	Nodal atmospheric boundary flows versus time, where *n* is the number of node with an atmospheric boundary type.
*root*_adt.dat	Concentration of sorbed species (mol $\text{kg}^{-1}_{\text{liquid}}$) versus time.
*root*_adx.dat	Concentration of sorbed species (mol $\text{kg}^{-1}_{\text{liquid}}$) versus space.
*root*_art.dat	Reactive surface of minerals (m^2 $\text{m}^{-3}_{\text{rock}}$) versus time. The minerals are specified by NWMIN and *W_MINERALS in the file *root*_trn.inp (chapter 4.5).
*root*_arx.dat	Reactive surface of minerals (m^2 $\text{m}^{-3}_{\text{rock}}$) versus space. The minerals are specified by NWMIN and *W_MINERALS in the file *root*_trn.inp (chapter 4.5).
*root*_bal.dat	Global mass balance of reactive transport components (mol)
*root*_che.out	Information on the chemical system
*root*_fit.dat	Volume fraction of the sum of all minerals (m^2 $\text{m}^{-3}_{\text{rock}}$) versus time.
*root*_fix.dat	Volume fraction of the sum of all minerals (m^2 $\text{m}^{-3}_{\text{rock}}$) versus space
*root*_gat.dat	Partial pressure of gaseous species (atm.) versus time. The gases are specified by NWGAS and *W_GASES in the file *root*_trn.inp (chapter 4.5).
*root*_gax.dat	Partial pressure of gaseous species (atm.) versus space. The gases are specified by NWGAS and *W_GASES in the file *root*_trn.inp (chapter 4.5).
*root*_gen.out	Information on general thermohydraulic system
*root*_iter.dat	Number of iterations required for reactive transport for each time step
*root*_mit.dat	Concentration of minerals (mol $\text{m}^{-3}_{\text{rock}}$) versus time. The minerals are specified by NWMIN and *W_MINERALS in the file *root*_trn.inp (chapter 4.5).
*root*_mix.dat	Concentration of minerals (mol $\text{m}^{-3}_{\text{rock}}$) versus space. The minerals are specified by NWMIN and *W_MINERALS in the file *root*_trn.inp (chapter 4.5).
*root*_out.out	Thermohydraulics results versus space. Its frequency is controlled by INTER and TIMEF described in card 10 and 13 of the file *root*_gen.inp (chapter 4.2).
*root*_pet.dat	pe versus time.
*root*_pex.dat	pe versus space.
*root*_pht.dat	pH versus time.
*root*_phx.dat	pH versus space.
*root*_sit.dat	Saturation index (ionic product divided by equilibrium constant) of minerals versus time. The minerals are specified by NWMIN and *W_MINERALS in the file *root*_trn.inp (chapter 4.5).
*root*_six.dat	Saturation index (ionic product divided by equilibrium constant) of

	minerals versus space. The minerals are specified by NWMIN and *W_MINERALS in the file *root*_trn.inp (chapter 4.5).
*root*_spct.dat	Concentration of aqueous species (mol kg^{-1}) versus time. The aqueous species are specified by NWCNC and *W_CONCENTRATIONS in the file *root*_trn.inp (chapter 4.5).
*root*_spcx.dat	Concentration of aqueous species (mol kg^{-1}) versus space. The aqueous species are specified by NWCNC and *W_CONCENTRATIONS in the file *root*_trn.inp (chapter 4.5).
*root*_sptt.dat	Total aqueous concentration of components (mol kg^{-1}) versus time. The aqueous species are specified by NWCOM and *W_COMPONENTS in the file *root*_trn.inp (chapter 4.5).
*root*_sptx.dat	Total aqueous concentration of components (mol kg^{-1}) versus space. The aqueous species are specified by NWCOM and *W_COMPONENTS in the file *root*_trn.inp (chapter 4.5).
*root*_tra.out	Information on transport parameters
*root*msh.dat	Output of the finite element mesh

4.10. Example of Input Files

Here the input files are given for the example described in chapter 5.1.

4.10.1. Example of file root.inp

```
Cal
    1    1    1    2
```

4.10.2. Example of file Cal_gen.inp

```
Calcite dissolution
   21   20    1    0    1    1
    1    4    0    1    1    3    4
    0    2
    0    1    0    0    0
    0    0    1    1    0    0    0
    0    0    0    0
        1.        1.        0.       25.       0.1
        0.  3160000.  3160000.  3160000.158000000.        1.
    0   10   20    0   20    2
    0.0001       0.0 1.000E-11       0.2
   -1
        0.        0.        0.
        0.  3160000.  3160000.  3160000.158000000.        1.
    1
    7Intrinsic permeabili    1
Intr.Perm.1st.princi        1.               Void        0.
Intr.Perm.2nd.princi        1.               Void        0.
Intr.Perm.3rd.princi        1.               Void        0.
  Reference porosity       0.1               Void        0.
```

```
    Minimum porosity        0.                  Void        0.
   15      Liquid density    1
   Reference density     1000.                  Void        0.
     Compressibility 1.000E-10                  Void        0.
Volumetric thermal e 1.000E-10                  Void        0.
    Solute variation 1.000E-10                  Void        0.
  Reference pressure        0.                  Void        0.
   16   Lliquid viscosity    1
Pre-exponential para 1.178E-09                  Void        0.
Exponential paramete        0.                  Void        0.
                Void        0.                  Void        0.
                Void        0.                  Void        0.
                Void        0.                  Void        0.
   -1
   -1
    1
Prescribed mass frac        0.
Prescribed gas flow         0.
Prescribed gas press        0.
Gamma coefficient fo        0.
Beta coefficient for        0.
Prescribed gas densi        0.
Prescribed mass frac        0.
Prescribed mass frac        0.
Prescribed liquid fl0.00006342
Prescribed liquid pr        0.
Gamma coefficient fo        0.
Beta coefficient for        0.
Void                        0.
Prescribed heat flow        0.
Prescribed temperatu        0.
Gamma coefficient fo        0.
Lambda coefficient f        0.
aq0 coefficient             0.
Delta parameter for         0.
Auxilay index (-1,1,         1
    2
Prescribed mass frac        0.
Prescribed gas flow         0.
Prescribed gas press        0.
Gamma coefficient fo        0.
Beta coefficient for        0.
Prescribed gas densi        0.
Prescribed mass frac        0.
Prescribed mass frac        0.
Prescribed liquid fl        0.
Prescribed liquid pr        0.
Gamma coefficient fo1000000000
Beta coefficient for        0.
Void                        0.
Prescribed heat flow        0.
Prescribed temperatu        0.
Gamma coefficient fo        0.
Lambda coefficient f        0.
aq0 coefficient             0.
Delta parameter for         0.
Auxilay index (-1,1,         1
   -1
   -1
```

```
   -1
   -1
```

4.10.3. Example of file Cal_gri.inp

```
    1    2    0
(5i5)
(2i5)
    1    1    1    1    2
    2    1    1    2    3
    3    1    1    3    4
    4    1    1    4    5
    5    1    1    5    6
    6    1    1    6    7
    7    1    1    7    8
    8    1    1    8    9
    9    1    1    9   10
   10    1    1   10   11
   11    1    1   11   12
   12    1    1   12   13
   13    1    1   13   14
   14    1    1   14   15
   15    1    1   15   16
   16    1    1   16   17
   17    1    1   17   18
   18    1    1   18   19
   19    1    1   19   20
   20    1    1   20   21
(i5,f10.0,i5,2i1,i3,2i1,f8.0)
(i5,30x,7i5)
    1        0.    0    1        0.    1    1    1    0    0    0    0
    2        5.    0    0        0.    1    0    1    0    0    0    0
    3       10.    0    0        0.    1    0    1    0    0    0    0
    4       15.    0    0        0.    1    0    1    0    0    0    0
    5       20.    0    0        0.    1    0    1    0    0    0    0
    6       25.    0    0        0.    1    0    1    0    0    0    0
    7       30.    0    0        0.    1    0    1    0    0    0    0
    8       35.    0    0        0.    1    0    1    0    0    0    0
    9       40.    0    0        0.    1    0    1    0    0    0    0
   10       45.    0    0        0.    1    0    1    0    0    0    0
   11       50.    0    0        0.    1    0    1    0    0    0    0
   12       55.    0    0        0.    1    0    1    0    0    0    0
   13       60.    0    0        0.    1    0    1    0    0    0    0
   14       65.    0    0        0.    1    0    1    0    0    0    0
   15       70.    0    0        0.    1    0    1    0    0    0    0
   16       75.    0    0        0.    1    0    1    0    0    0    0
   17       80.    0    0        0.    1    0    1    0    0    0    0
   18       85.    0    0        0.    1    0    1    0    0    0    0
   19       90.    0    0        0.    1    0    1    0    0    0    0
   20       95.    0    0        0.    1    0    1    0    0    0    0
   21      100.    0    2        0.    1    0    1    0    0    0    0
    1             0.
    2             0.
    3             0.
    4             0.
    5             0.
    6             0.
```

```
    7             0.
    8             0.
    9             0.
   10             0.
   11             0.
   12             0.
   13             0.
   14             0.
   15             0.
   16             0.
   17             0.
   18             0.
   19             0.
   20             0.
   21             0.
    1            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
    2            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
    3            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
    4            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
    5            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
    6            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
    7            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
    8            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
    9            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   10            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   11            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   12            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   13            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   14            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   15            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   16            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   17            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   18            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   19            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
   20            0.1 0.00000000E+00 0.00000000E+00 0.00000000E+00
    0
    0
    0    5
    0
    0
    0
```

4.10.4. Example of file Cal_trn.inp

```
! Transport file for calcite dissolution

*OPTIONS

TITLE=CalciteDissolution
IOPFLU= 0
IOPGASTR= 0
IOPUNITSMIN= 1
IOPSI= 1
IOPDIFMOL= 0
IOPTORL= 0
IOPTORG= 0
IOPSATINNODES= 0
```

```
ISWITCH= 0
NJACOB= 1
IOPBGPUNITS= 0
IOPGASSOURCE= 1
IOSOLU= 0
IOPBCL= 3
IFLAGK0= 0

*PARAMETERS

THETATRA= 1
MAXITPTR= 100
TOLTR= 0.0001
MAXITPCH= 30
TOLCH= 0.0001
MAXITPAD= 30
TOLAD= 0.0001
MAXDIVERG= 3
FAC_UPD= 10

*DIMENSIONS

NTIMINT= 1
NWXY= 10
NWDIM= 2
NWTI= 1
NWNOD= 11
NWCOM= 2
NWMIN= 1
NWCNC= 0
NWGAS= 0

*TIMEINCREMENTS
    1158000000.   50        1.        2.        2.

*W_COMPONENTS
    1    2

*W_MINERALS
    1

*W_NODES
    1    3    5    7    9   11   13   15   17   19   21

*LIQ_BOUNDARYCONDITIONS
    1    2    1        0.

*MATERIAL_PROPERTIES
    1      0.     10.     10.

*END_DATA
```

4.10.5. Example of file Cal_che.inp

```
'TITLE OF THE PROBLEM : Calcite dissolution'
'-----------------------------------------'
'DEFINITION OF THE GEOCHEMICAL SYSTEM'
```

```
25           0    !initial temp. of the system
'PRIMARY AQUEOUS SPECIES'
'ca+2'
'co2(aq)'
'h+'
'*'
'AQUEOUS COMPLEXES'
'caco3(aq)'
'cahco3+'
'caoh+'
'co3-2'
'hco3-'
'oh-'
'*'
'MINERALS'
'calcite'      1
'*'    0
'GASES'
'*'
'SURFACE COMPLEXES'
'*'
'-------------------------------------------------------------------'
'INITIAL AND BOUNDARY WATER TYPES
1     1    0    !niwtype, nbwtype, nrwtype= number of ini, bound, rech
waters
1  25
'          icon        guess         ctot          constrain'
'co2(aq)'    1         1.99E-05      1.00E-03       ' '
'ca+2'       4         9.71E-04      9.87E-04       'calcite'
'h+'         3         1.05E-08      1.05E-08       ' '
'*'          0          0.0           0.0          ' '
1  25
'          icon        guess         ctot          constrain'
'co2(aq)'    1         3.00E-05      3.00E-05       ' '
'ca+2'       1         4.00E-05      4.00E-05       ' '
'h+'         3         1.00E-03      1.00E-03       ' '
'*'          0          0.0           0.0          ' '
'---------------------------------------------------------------------'
'INITIAL MINERAL ZONES'
1
1
'mineral         vol.frac.   area'
'calcite'          .5         .14
'*'               0.0       0.0
'---------------------------------------------------------------------'
'INITIAL SURFACE ADSORPTION ZONES'
0
'---------------------------------------------------------------------'
'end'
```

4.10.6. Example of file Master25.dat

```
'temp' 1 25.0
'ca+2'  6  2
'h+'  9  1
'hco3-'  4 -1
'null'     0   0
```

```
'co2(aq)'  2  1 'h+'  1 'hco3-' -6.3447  3  0
'caco3(aq)'  3  1 'ca+2' -1 'h+'  1 'hco3-'  7.0017  0  0
'cahco3+'  2  1 'ca+2'  1 'hco3-' -1.0467  4  1
'caoh+'  2  1 'ca+2' -1 'h+'  12.85  4  1
'co3-2'  2 -1 'h+'  1 'hco3-'  10.3288  5 -2
'oh-'  2  1 'h2o' -1 'h+'  13.9951  3 -1
'null' 1 0. '0' 0. 0. 0.
'calcite'  36.934  3  1 'ca+2' -1 'h+'  1 'hco3-'  1.8487
'null' 0. 1 0. '0' 0.
'null' 0. 0. 1 0. '0' 0.
'null' 1 0. '0' 0. 0.
```

4.10.7. Example of file Kinetics.dat

```
'calcite'  1  15  2 'Inskeep and Bloom, 1986'
      2.25E-09  1  1  0
'null' 0 0.0 0.0 ' '
```

5. Tutorial for VisualRetraso

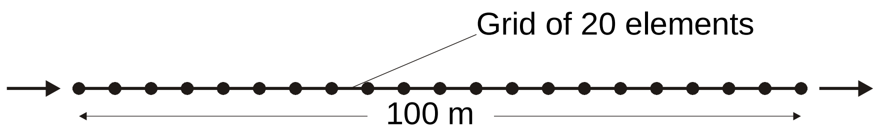
This tutorial is not aimed at giving a global vision of VisualRetraso, neither to show how to perform certain tasks. Instead, it wants to give a fast introduction by describing all the actions that have to be carried for a simple 1D example, explained in chapter 5.1.

5.1. Description of the Example

The example treats the dissolution of calcite by subsaturated infiltrating water in a one-dimensional domain of 100 m length divided into 20 elements (see figure below). Initially the water is saturated with calcite, has a pH of 8 and a total inorganic carbon concentration of 10^{-2} mol/kg. The infiltrating water has a total inorganic carbon concentration of 3×10^{-5} mol/kg, a total calcium concentration of 4×10^{-5} mol/kg and a pH of 3. The water flux is 2 m/year (=6.342×10^{-5} kg m^{-2} s^{-1}), the porosity is 0.1 and the dispersivity is 10 m. The calcite dissolves kinetically according to the following rate law:

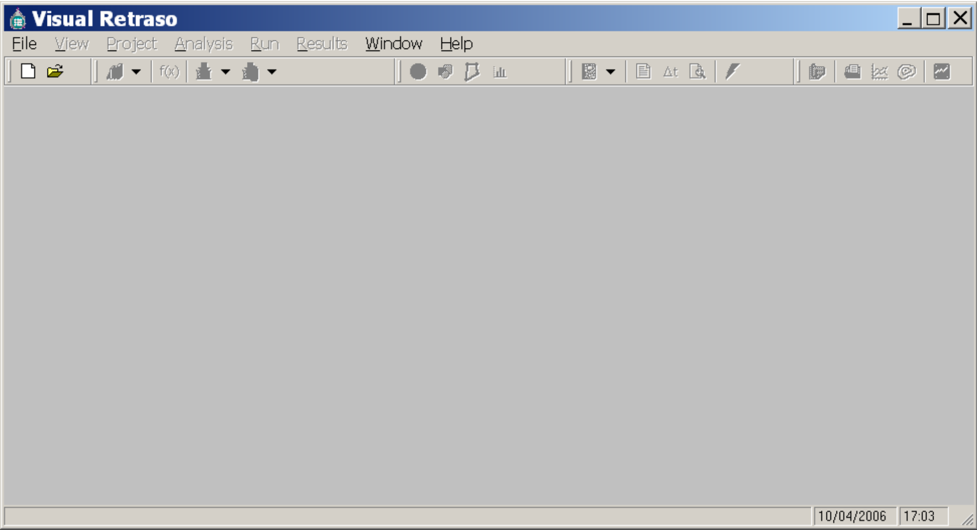
$$r_{cal} = 2.25\times10^{-9}\sigma_{cal}\left(\Omega_{cal} - 1\right)$$

The initial reactive surface is 0.14093 m^2 m^{-3}. The time to be simulated is 5 years (= 1.577×10^{8} s).



5.2. Starting the Program

Execute the program "VGUM". The following window will appear.

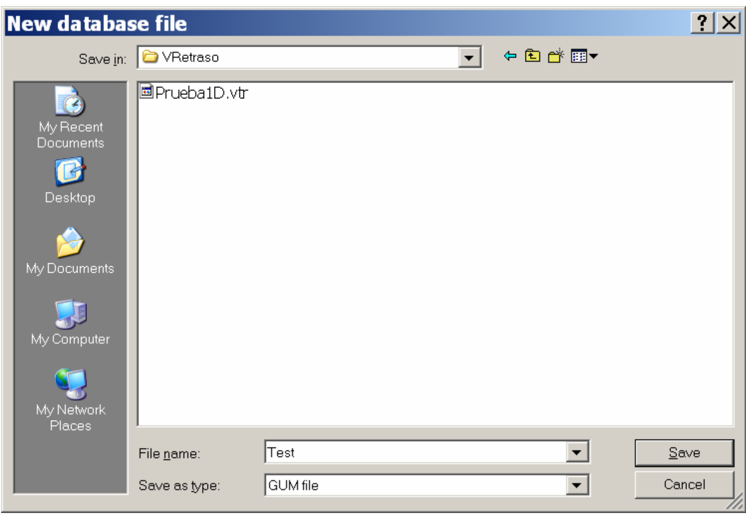


Before showing this window the program may show a message saying that one must change in the regional configuration the decimal symbol for number and money to "." (dot). If this configuration is not activated, VisualRetraso will not work.

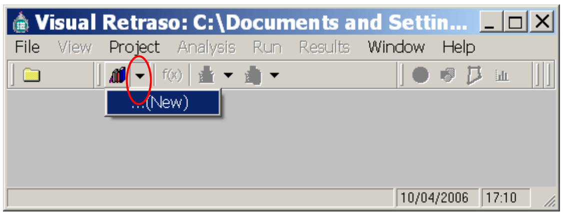
Be sure that the menu is shown in English. If not, it must be changed by entering the language option: "Archivo > Idioma > Inglés" (if it is in Spanish).

5.3. Creating a Project

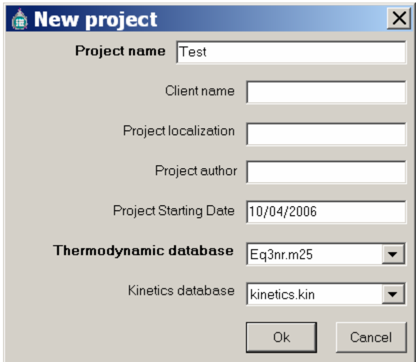
Next, we create a new project by means of the option "file > New Database...". Carrying out this action, the program asks for the filename by showing the typical Windows file explorer. In this file all data of the project (input and output data) will be saved. If the file already exists, a message will appear that asks for a confirmation for overwriting the old file. In the figure below we called the filename "test", to which the program will automatically add the extension ".vtr".



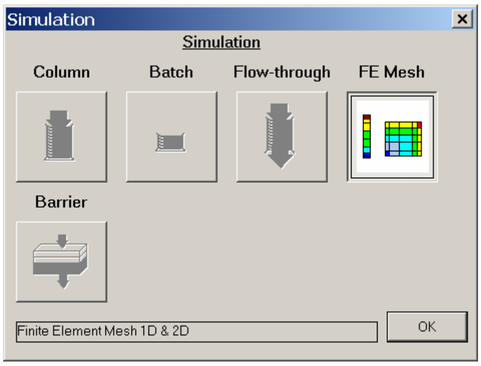
Once a valid filename has been given, we must create a new project. For this, click on the dropdown next to the "project list" button (indicated by the red circle) and select "new".



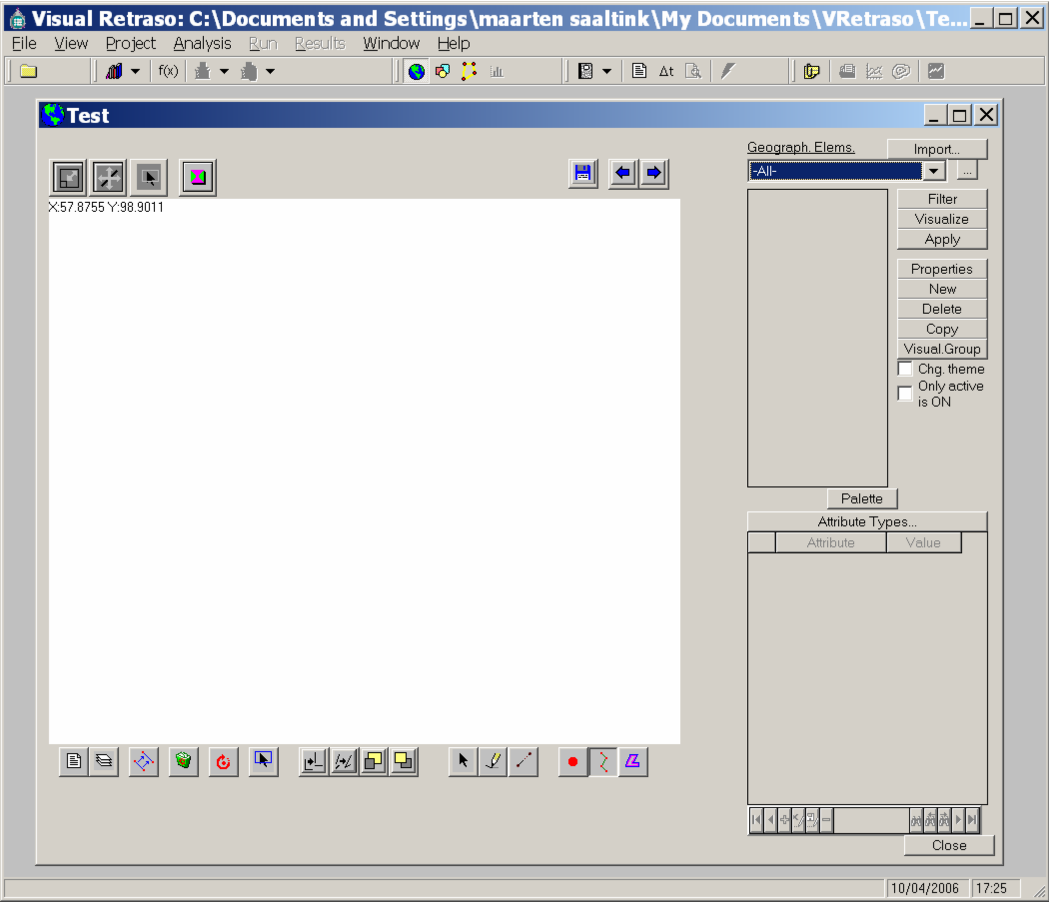
A window appears where we can specify the data of the project (name, thermodynamic database, kinetic database, localization, date and author).



At least one must give a project name, the thermodynamic database and the kinetic database. Click on "Ok" to continue. One is asked for the type of simulation. Only the "FE mesh" is operational. So, we select this option and click on "OK".



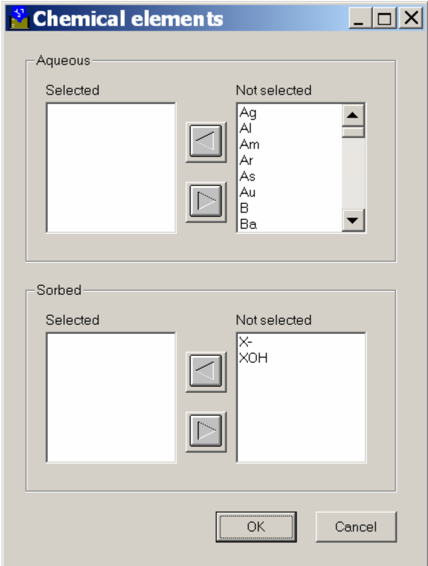
Automatically the program creates an analysis associated to the present project. A window appears for geography/geometry.



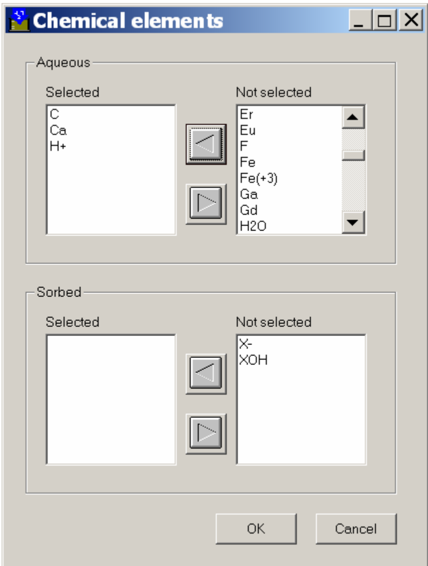
After having carried out the previous steps, the project has been correctly created and initialized. As a result, new options appear in the menu, that will be used (partly) during this tutorial.

5.4. Definition of the Chemical System

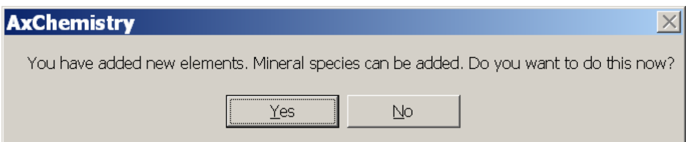
For the definition of the chemical elements of the chemical system choose the menu option "project > chemical elements". The following window will appear:



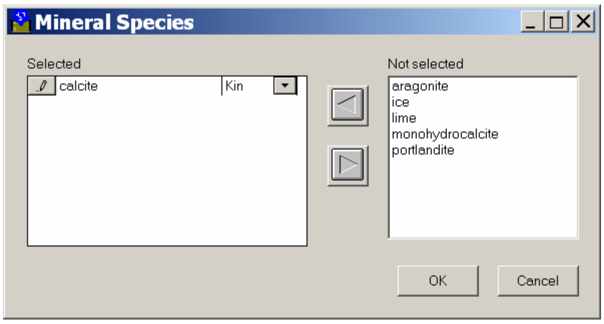
Elements can be selected by selecting them form the list "not selected" and clicking on the button , which will make them appear in the list "selected". Vice versa, elements can be deselected by selecting them from the list "selected" and clicking on the button , which will make them appear in the list "not selected". In this way select the elements "C", "Ca" and "H+":



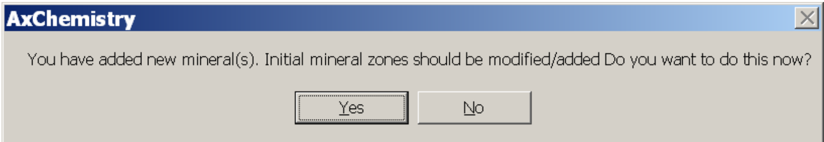
When clicking on "OK", the program asks whether we want to add minerals,



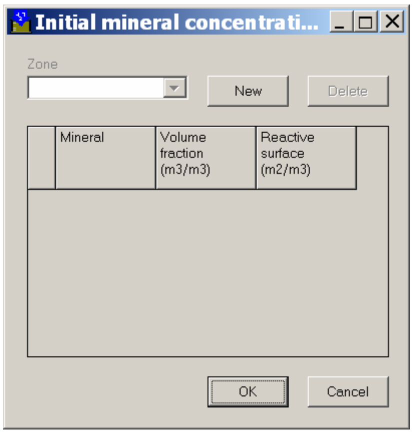
to which we answers affirmatively. With the same buttons and minerals can be selected and deselected. Moreover, for each mineral it is needed to say whether they are in equilibrium or kinetic. Select the mineral "calcite" with "kinetic" as shown below.



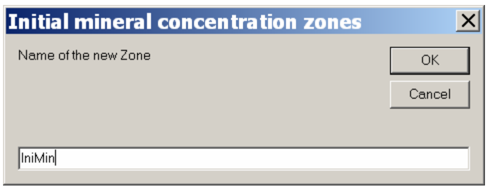
When clicking on "OK" the program asks whether we want to add/change mineral zones, to which we answer affirmatively.



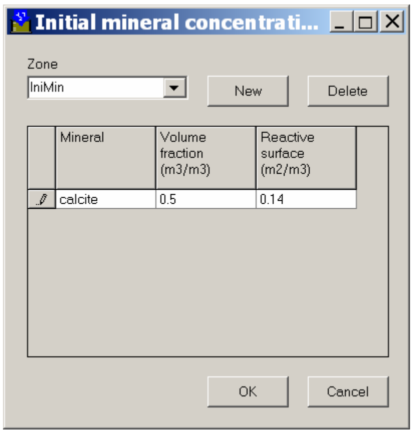
The next window appears:



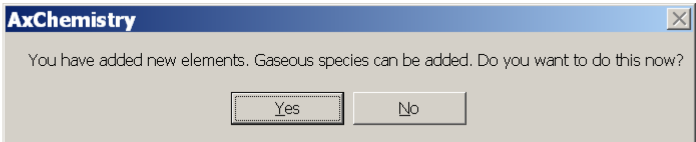
Click on "new" to create a new mineral zone. The program asks for the name of the zone. Give a name and click on "OK".



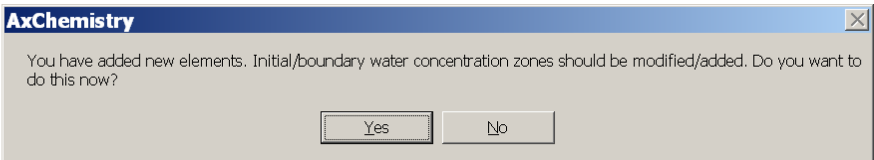
A window will appear at which we modify the data as shown in the following figure:



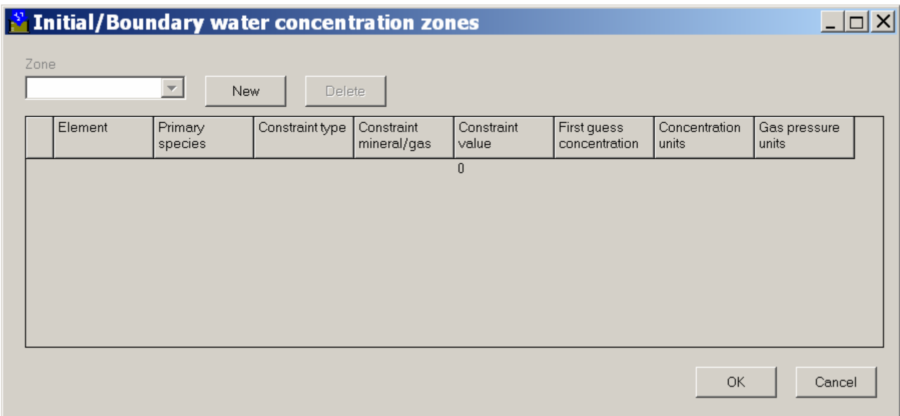
When clicking on "OK" the program asks whether we want to add gaseous species,



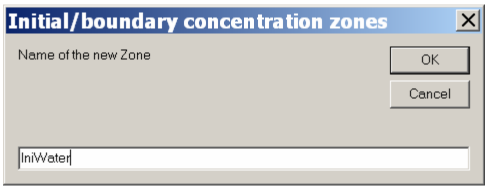
to which we answer "NO". The program asks whether we want to add initial/boundary water zones



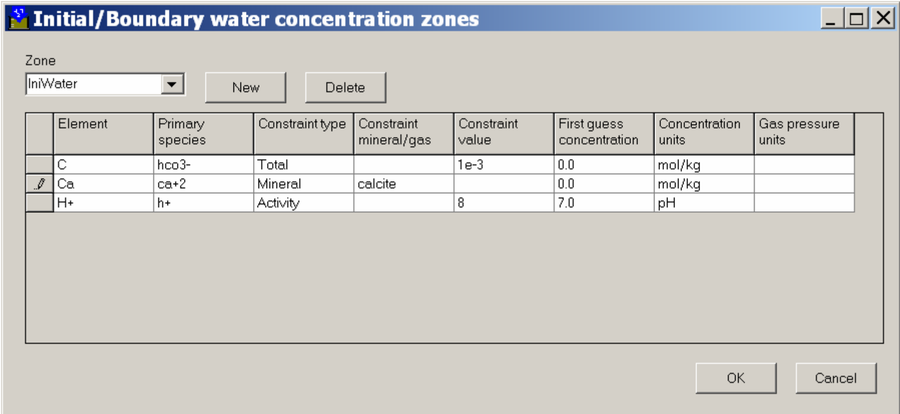
to which we answer affirmatively. The following window will appear:



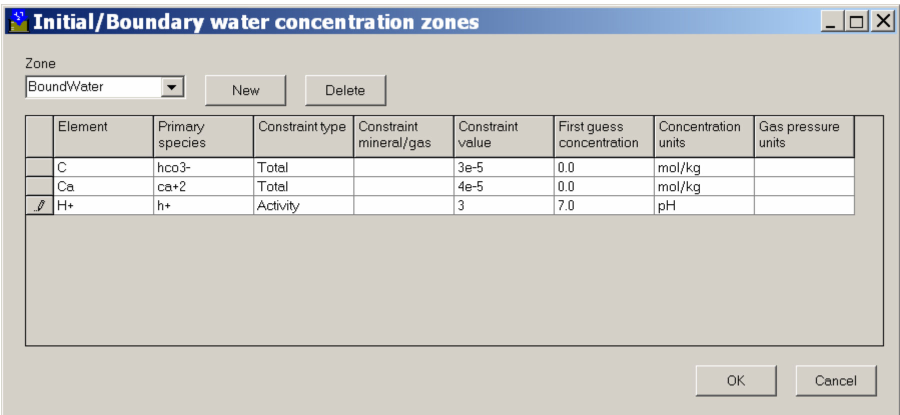
First create a new water zone by clicking on "New". The program asks for a name for the new zone. Give a name and click on "OK".



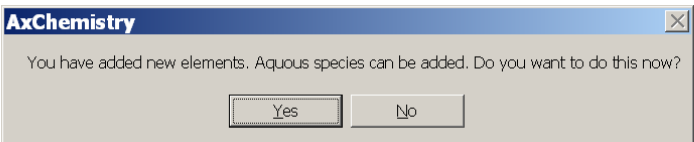
A window appears at which we modify the data as shown in the following figure:



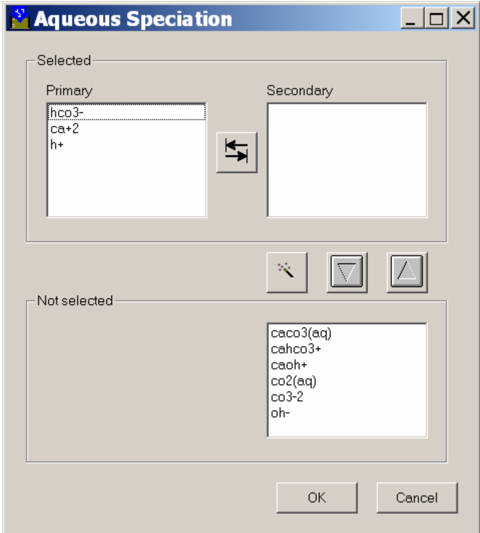
Then, we create another zone clicking on "New". The program asks for a name for the new zone. Give a name and click on "OK". We modify the data of this second zone as shown in the following figure:



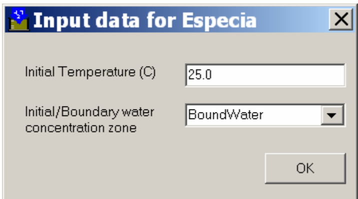
The program asks, whether we want to add aqueous species,



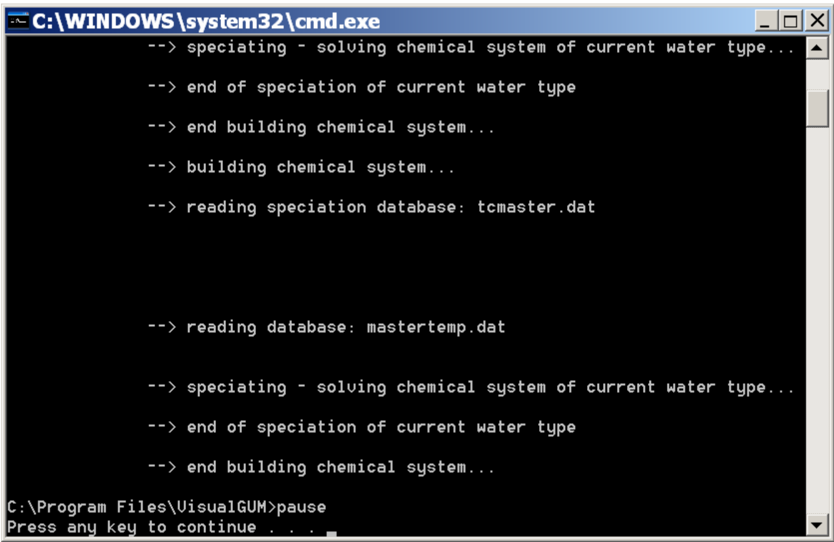
to which we answer affirmatively. The following window will appear:



We can select and deselect aqueous species manually by means of the buttons and . However, in this tutorial we select them automatically by means of the button . The program asks with what temperature and with what water zone we want to speciate. Answer as shown below:

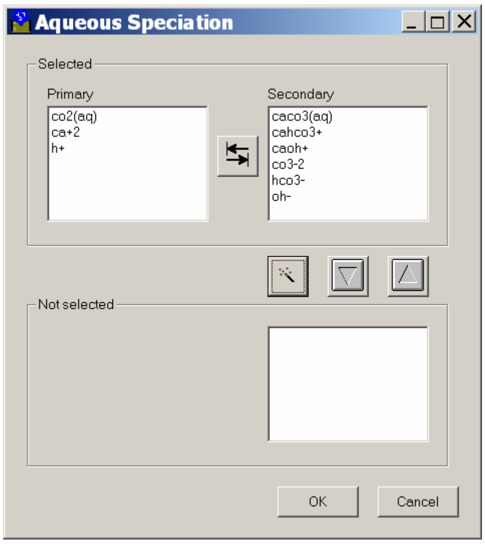


When clicking on "OK", a speciation program will be run through a window with a black background, where messages from the speciation program can be seen.

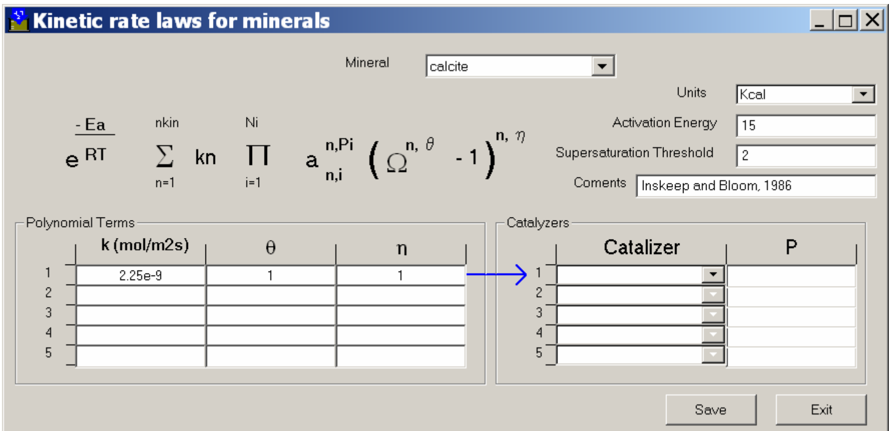


When this program finishes, a message is shown in the window with the black background saying "Press any key to continue". When doing so primary and secondary species are shown, that are selected by the speciation program. Moreover, the speciation

program has changed the values for the "first guess concentration" of the window for "initial/boundary water concentration".



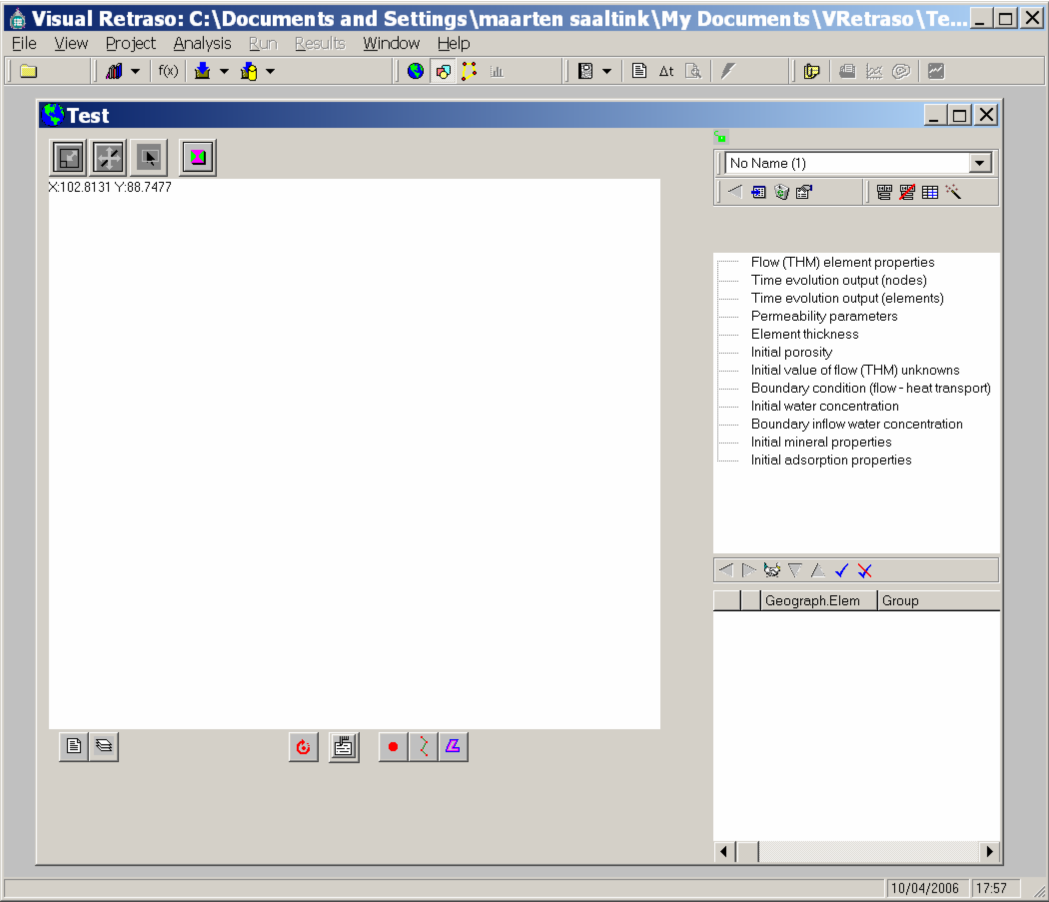
Click on "OK" to accept the aqueous species. The chemical system has now been defined. If one wants to view or change chemical data, one can do so by means of "Project > chemical species", "Project > Chemical zones" and "Project > Chemical constants". We end the definition of the chemical system by changing the rate law by means of "Project > Chemical constants > Kinetic". Then a window appears that permits us to change the kinetic parameters of the only mineral (calcite). Change these parameters as is indicated in the next figure ("Supersaturation threshold" and "k(mol/m2/s)").



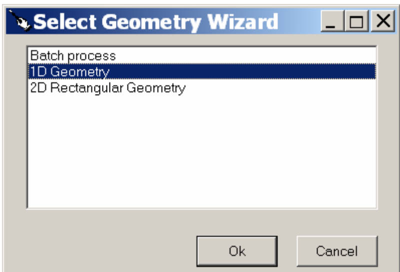
Click on "Save" and "Exit".

5.5. Definition of the Geometry

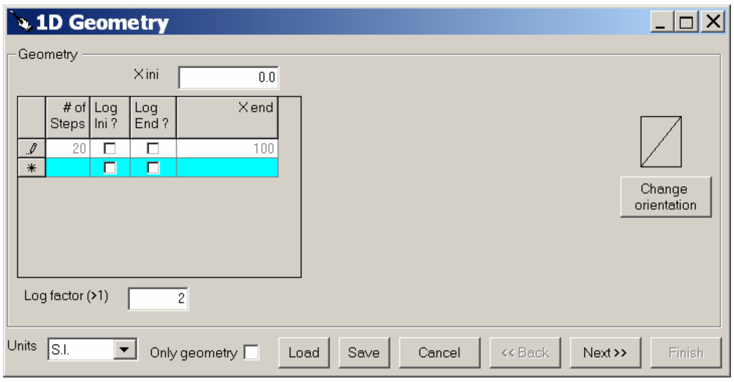
For the definition of the geometry go to "View > Zonation"



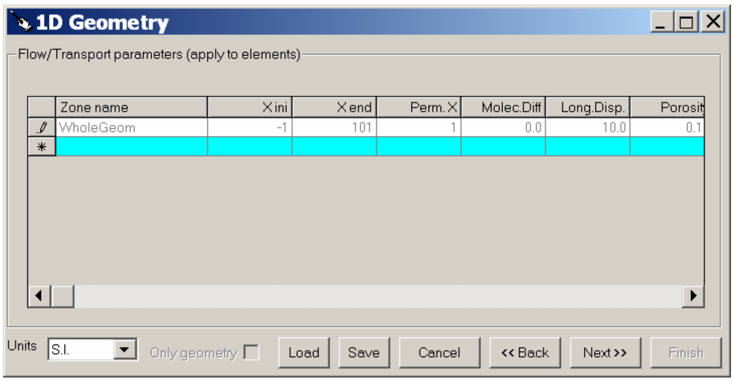
We will accelerate the process of entering data by using the wizard button  situated below a drop-down with the name of the analysis (in this case with the default name "No name(1)"). This wizard allows the creation of simple geometries and grids. In this tutorial we choose "1D Geometry",



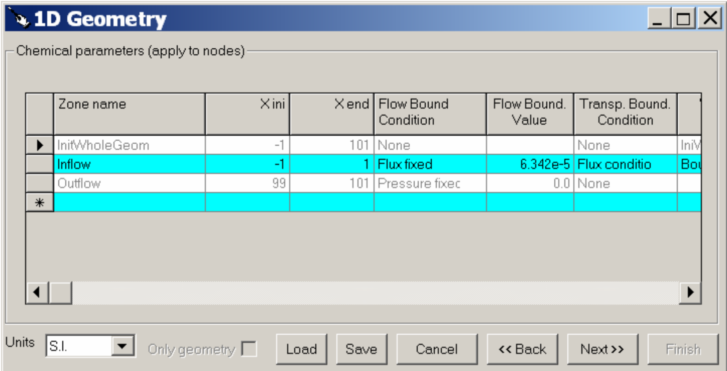
upon which a window appears at which we must enter the following information: at "# of steps" the value 20 (number of elements), and at "X end" the value 100 (length of the domain). For the rest of the values we take the default values. The screen must be like the following figure:

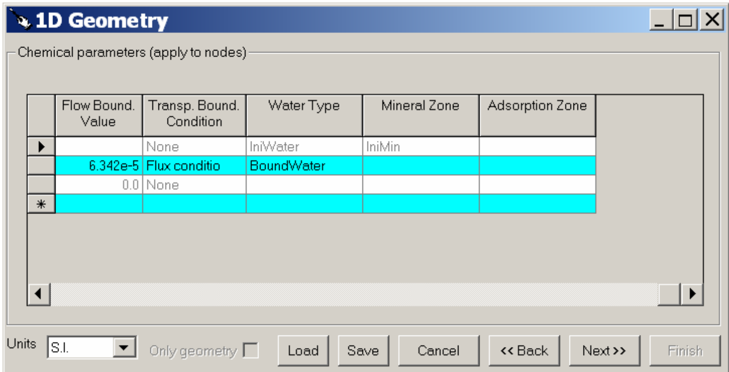


Click on "Next", what allows us to enter the values for flow and transport parameters as shown in the following figure. By default the program creates a zone "WholeGeom" that covers the whole domain and is used to enter the values for permeability ("Perm X" value 1.0), molecular diffusion coefficient ("Molec.Diff" value 0.0), dispersivity ("LongDisp" value 10) and porosity ("Porosity" value 0.1). Make sure that "Units are "S.I.".

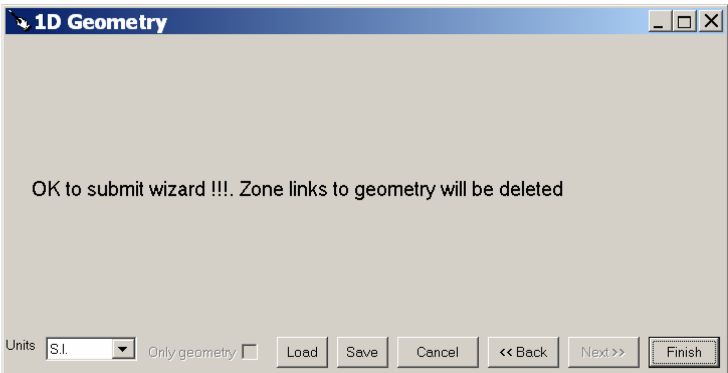


By again clicking on "Next", a window appears for the assignment of initial and boundary conditions. By default a zone "InitWholeGeom" is created in the first record, which covers the whole geometry and which is where initial values are assigned at "Water Type" with the value "IniWater". The program has already assigned other values by default. Moreover, we have to insert two other records corresponding to the boundary conditions at both ends of the domain with the names "InFlow" and "OutFlow" (or other names). The two following figures show the same window with two different horizontal scrolls, so that all columns can be seen. As can be observed at the first node (with coordinate 0 and, therefore, between, for instance, -1.0 and 1.0) a fixed flux is applied with a value of $6.342 \cdot 10^{-5}$ kg m^{-2} s^{-1} (= 2 m/year), a flux condition for transport and a water type named "BoundWater". For the last node (of coordinate 100 and, therefore, between, for instance, 99.0 and 101.0) a fixed pressure of 0.0 is applied with a natural transport boundary condition (i.e., none and without a water type).



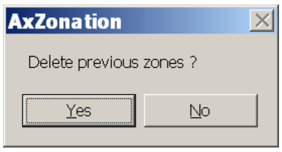


When clicking for the last time on "Next" the program informs us that the wizard has finished the data input.

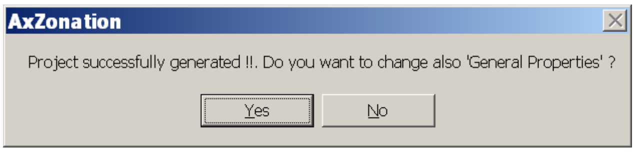


To start the filling of the database with the specified data, we click on "Finish". A message informs us of the successful generation of the new mesh.

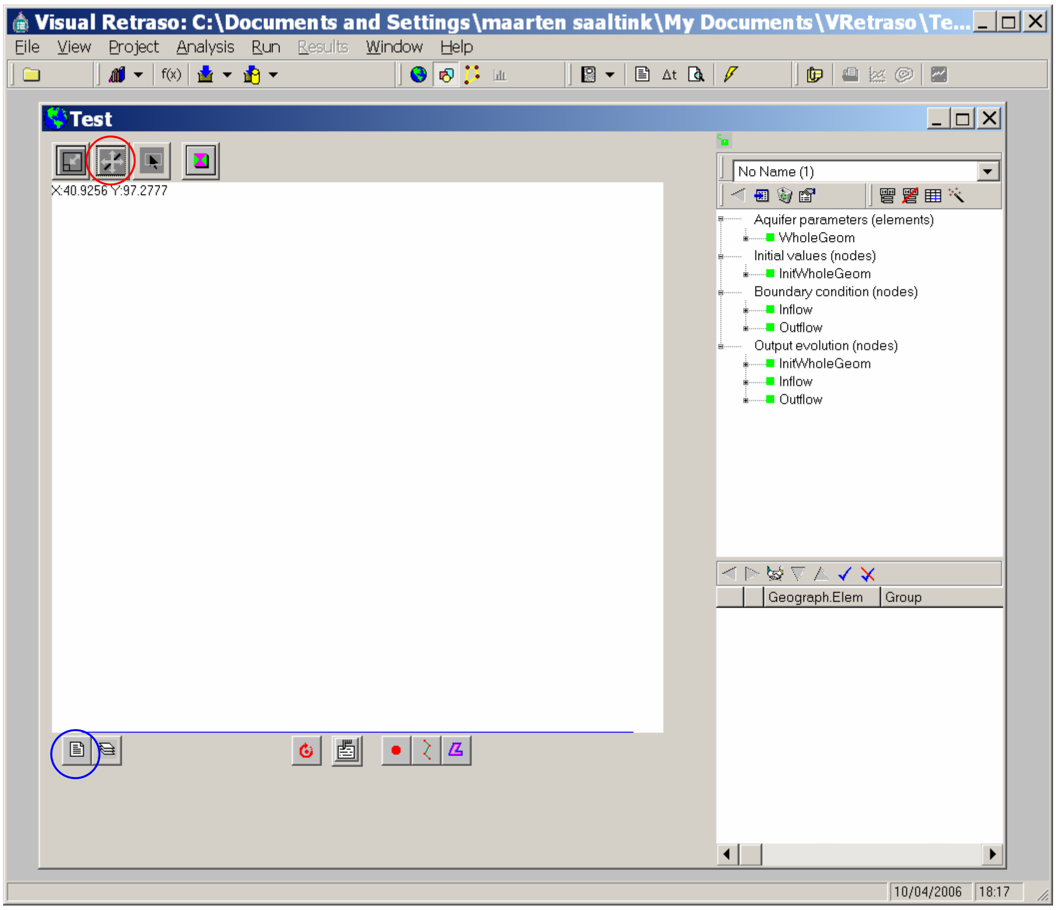
Then, a message is shown warning us that all previous zone information is deleted, to which we answer affirmatively.



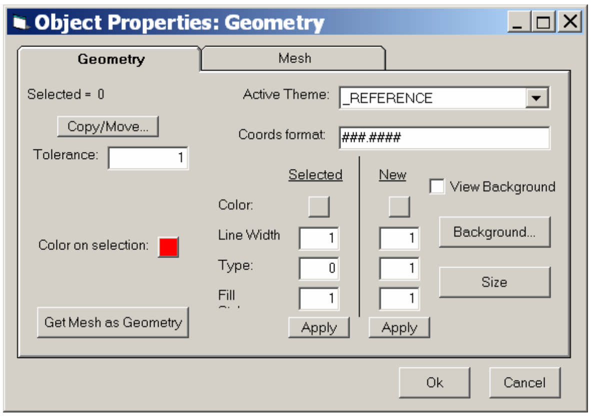
Finally, the program informs us of the success of the operation and asks whether we also want to update the general properties, to which we answer affirmatively too.



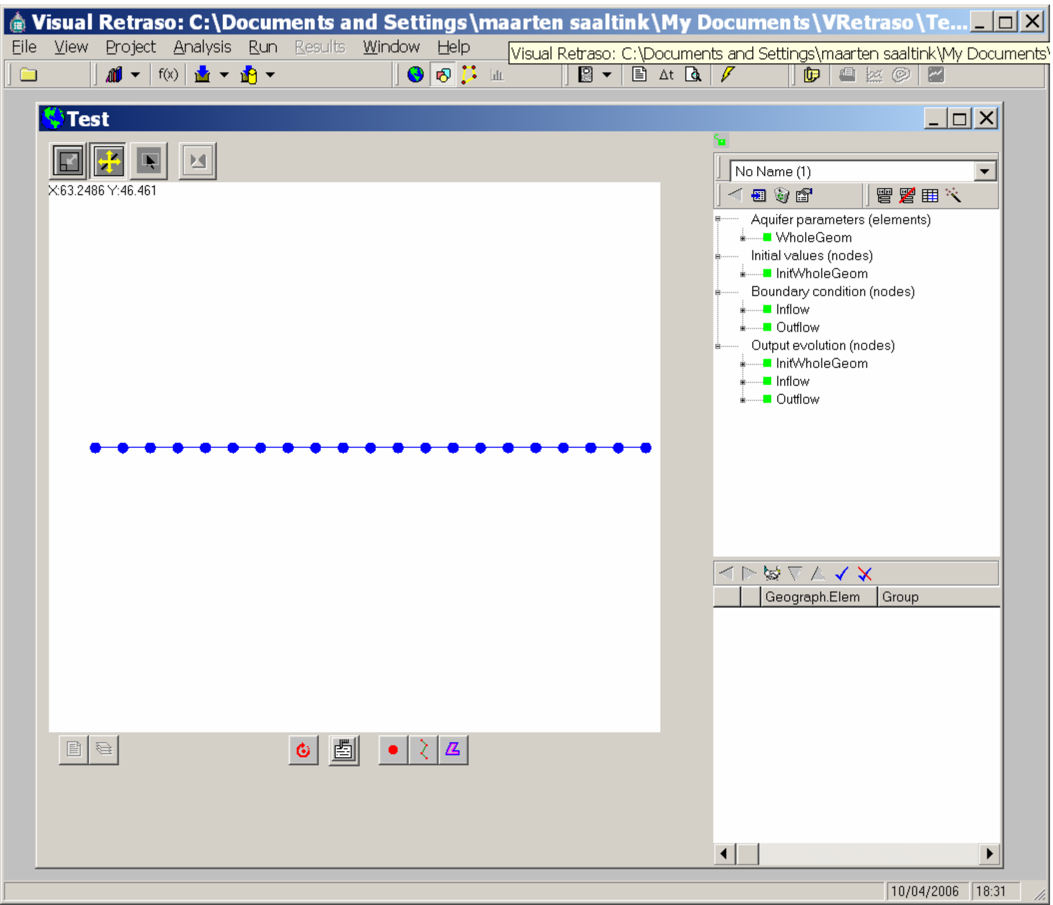
As a result a new geometry appears on the screen as shown below.



The generated mesh is shown at the bottom of the figure. After clicking the pan button (red circle) we can drag the mesh upwards. Moreover, we can increase the size of the nodes by means of the "show properties" button (blue circle). This permits to change the tolerance (which also controls the size of the nodes) from 0.1 to 1.



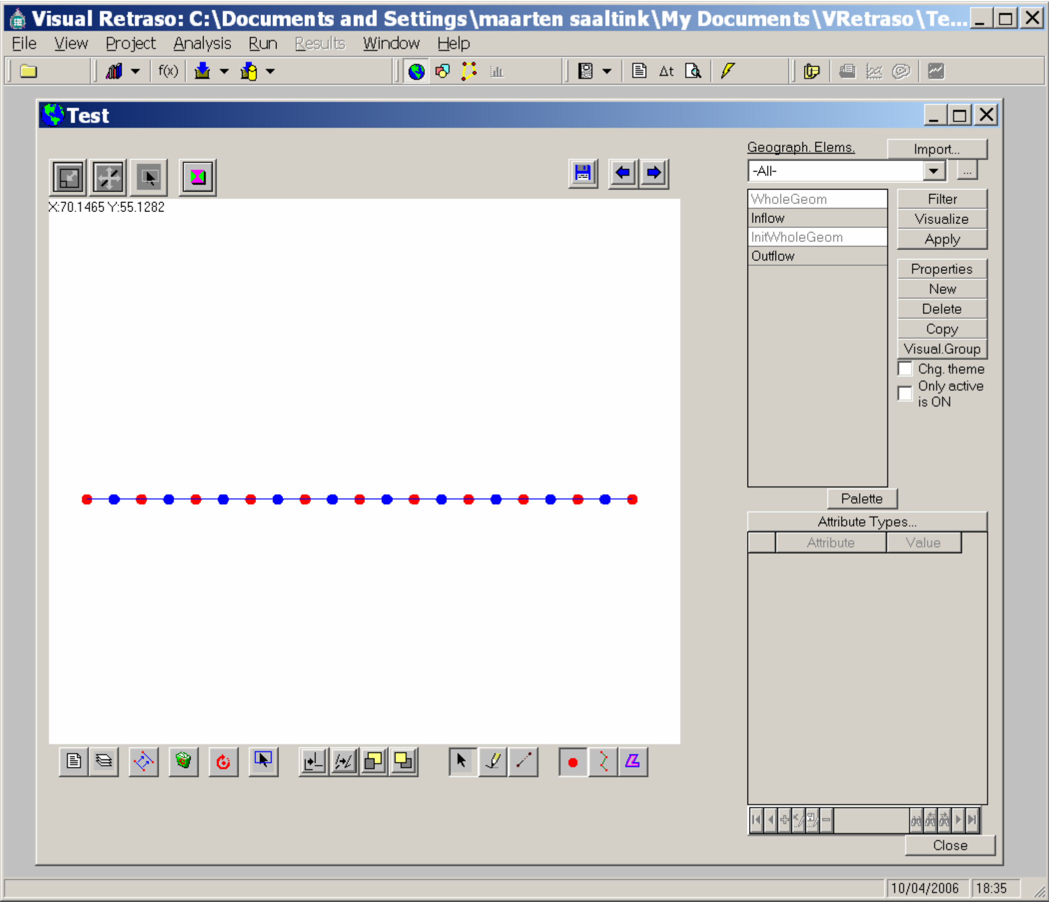
This will give the following picture



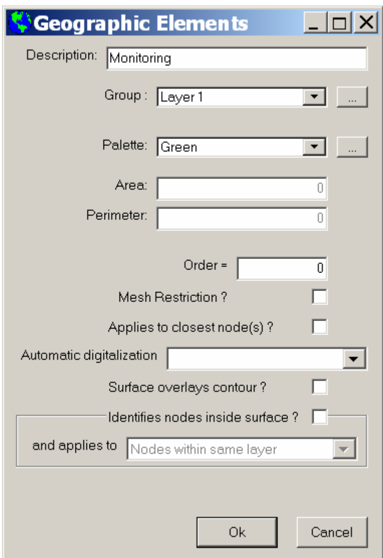
5.6. Creating Zones for Results

We now go to the geometry window by means of the option "View > Geometry". We select the points of which we want to know the evolution in time. To do so, make sure that the buttons  and  are activated. These buttons permit the selection of points. Select with the cursor alternating points as shown in the figure below. Errors can be

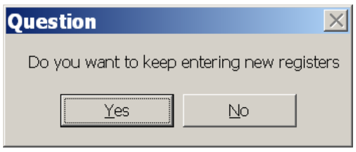
corrected either by selecting again an already selected point (which deselect it) or by clicking on the button , which deselects everything.



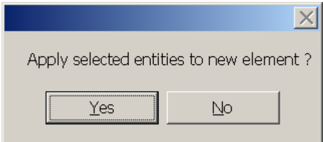
Then click on "New" to add a geographical element. A window is opened to give a name to the new element as is shown in the figure below. In this figure one can see that the new element is called "monitoring" and that the colour "green" has been assigned to it.



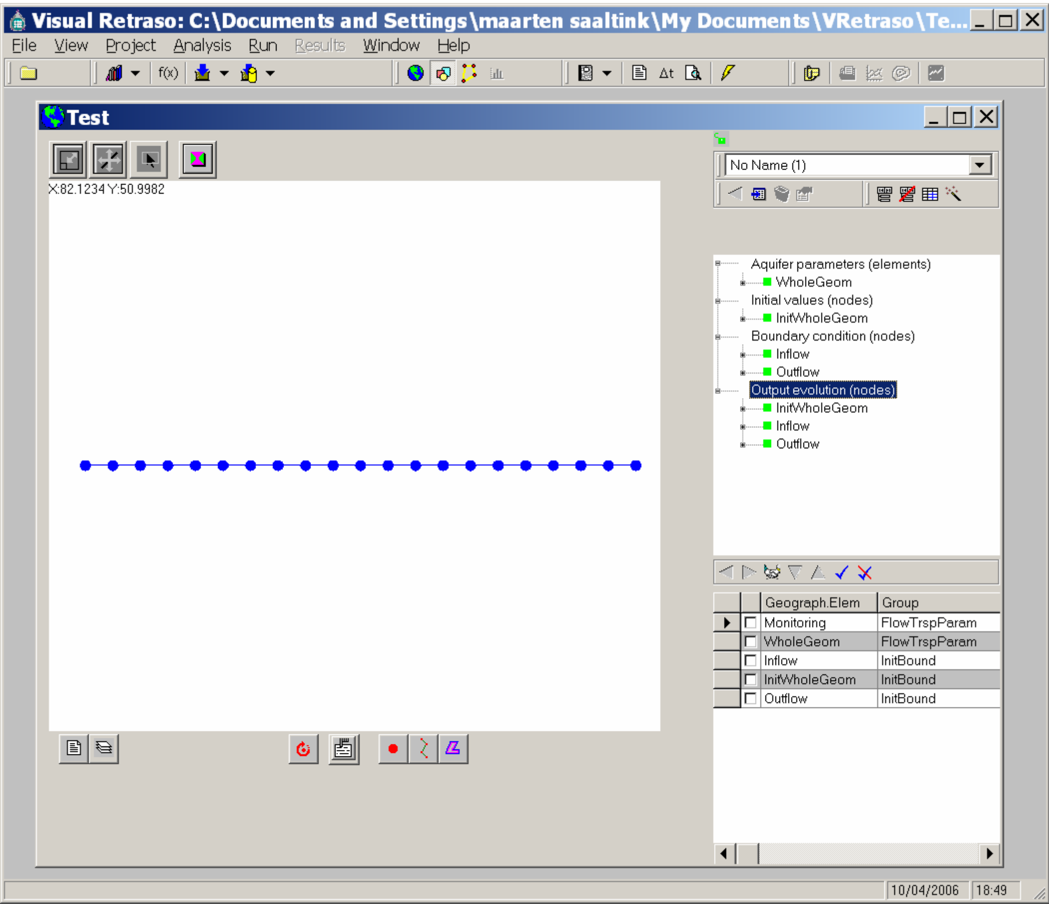
When clicking on "OK", a message appears asking us, whether we want to add new zones, to which we answer "No"



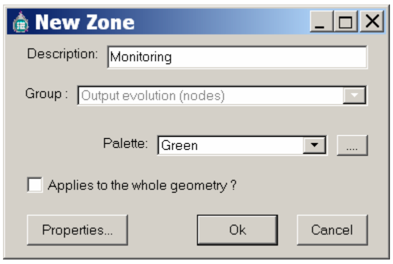
As still some points are being selected, the program asks whether we want these selected points to pertain to this new geographical element that we just created. Answer affirmatively.



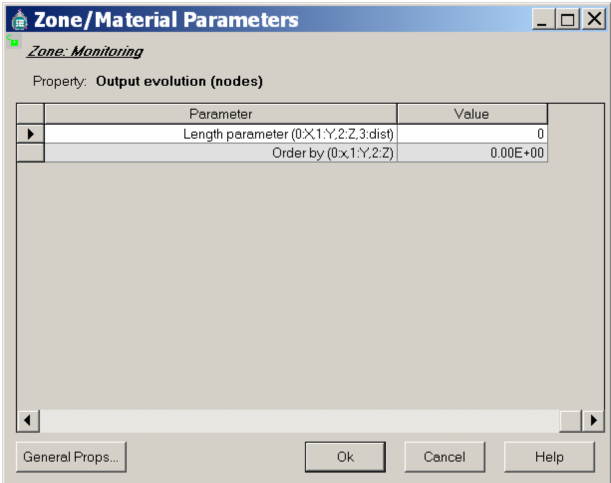
We now go to the zonification window by means of "View > Zonation" and create a new zone to which we will assign the previously created geographical element. To do so, select "Output evolution nodes" and click on the button (Add new Zone) as shown in the next figure



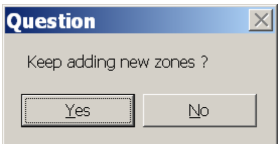
Then we add the name of the zone, which in this case coincide with the name of the geographical element ("monitoring"), select a colour (e.g., green) and click on "OK".



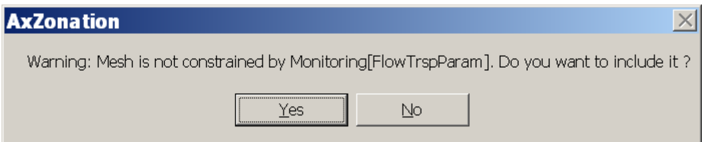
The program asks us the parameters for this zone. We accept the default values by clicking on "OK".



When the program asks us whether we want to add new zones, we answer "No".



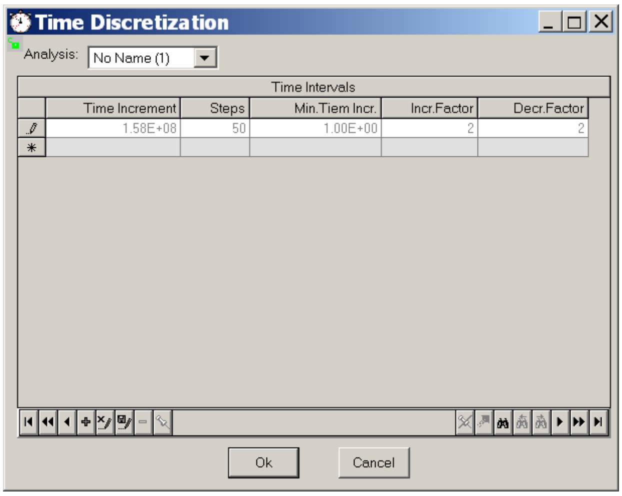
We have to select the zone "Monitoring" and the geographical element with the same name. When the button "Match names"  is activated, selecting a zone will automatically select a geographical element with the same name. Then click on the button  to assign the geographical element to the zone.



The program warns us, that the geographical element does not constrain the grid, to which we answer affirmatively.

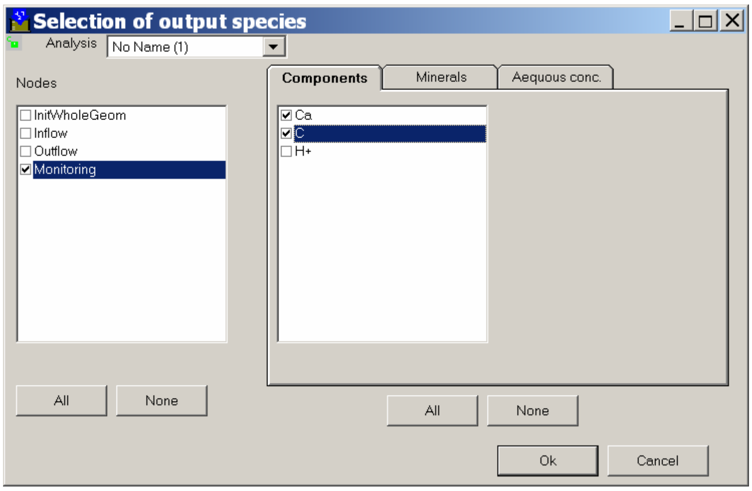
5.7. Temporal Discretisation

To define the temporal discretization we go to the option "Analysis > Temporal discretization" and fill the fields as indicated by the figure, followed by clicking on "OK".

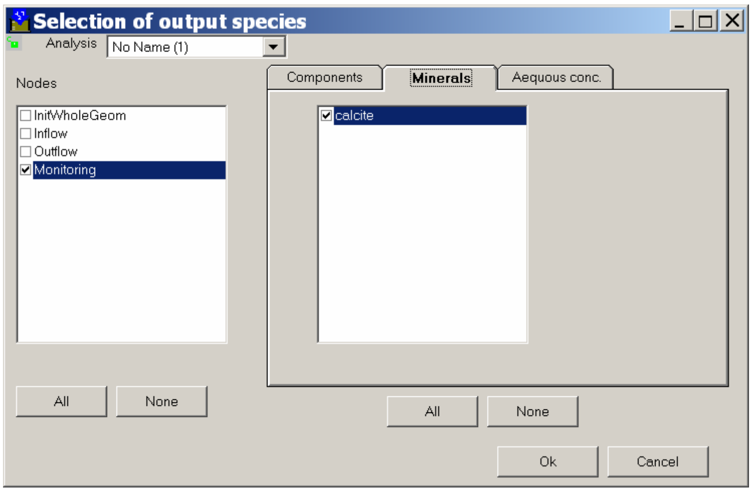


5.8. Selection of Results

Next, we will select what chemical output we want to have and at what nodes. For this, go to the option "Analysis > Select output species". The window, that appears, is shown in the next figure. We select the node zone "Monitoring" (created in chapter 5.6) and the components as indicated in the next figure.



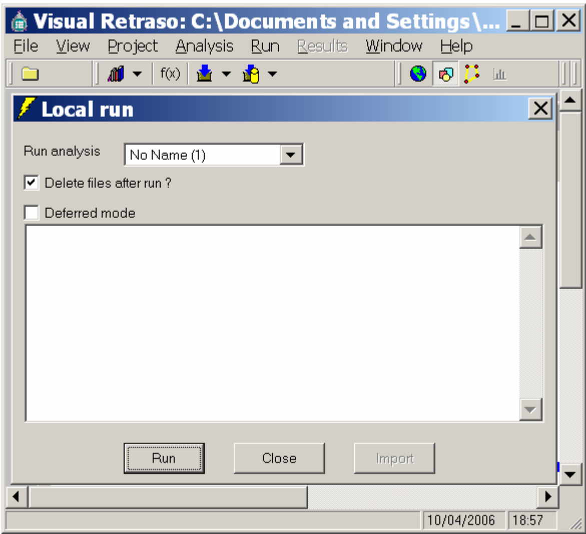
In the tab called "minerals" we also select the only available mineral as indicated below.



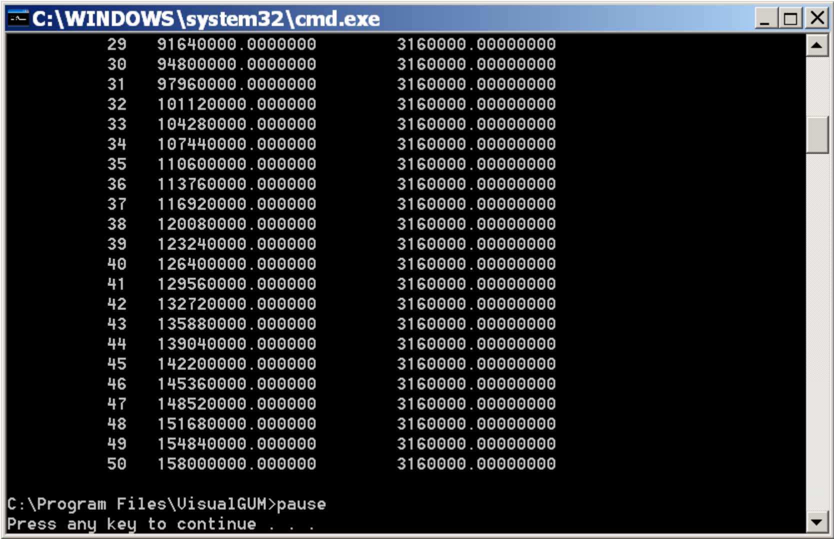
As we do not select aqueous species, we finish this part by clicking on "OK".

5.9. Running

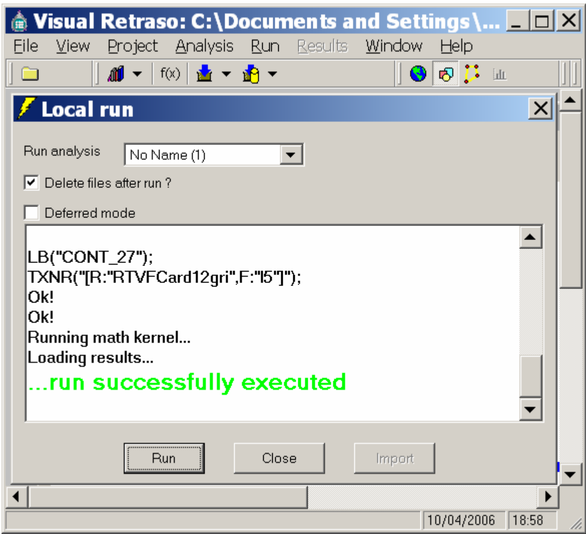
We now can run the example by going to the option "Run > Local".



In the window that appears, we directly click on the button "Run". Previous to the running the program checks certain consistencies of the input data and shows the result in a window. Then the reactive transport program is run, showing a window with a black background. When the reactive transport calculations have finished, this window shows a message "Type any key to continue".



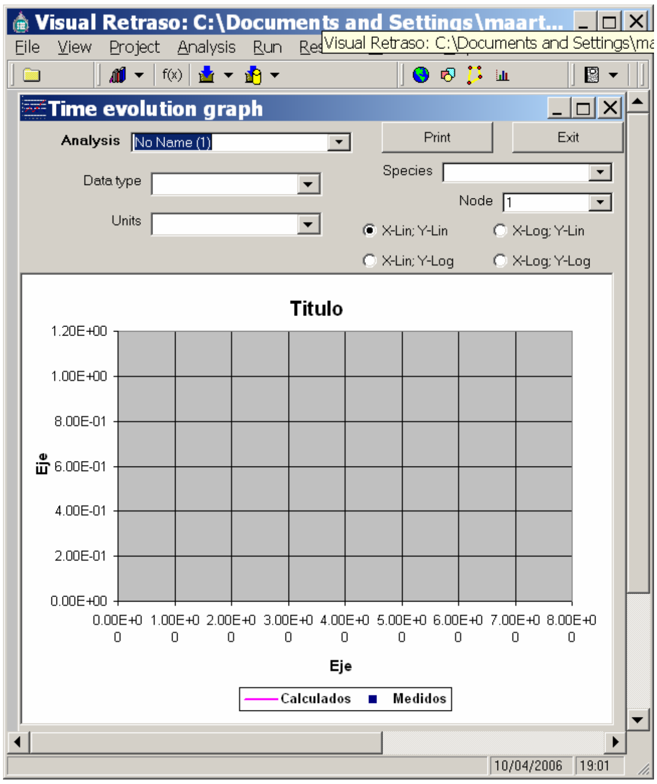
When we type any key, the window disappears and a message is shown informing us that the program was run succesfully.



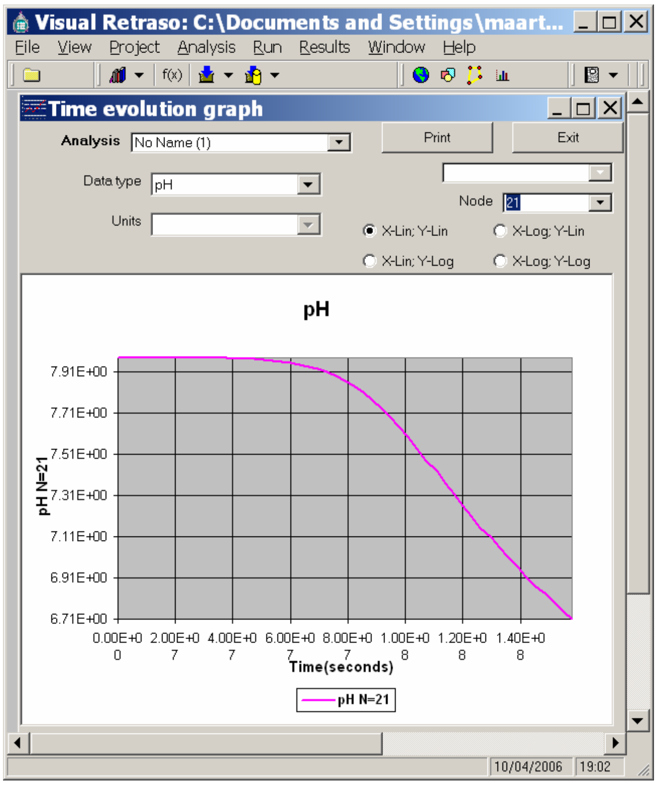
We close the last window by clicking on "Close".

5.10. Viewing Results

Various types of results can be viewed. In this tutorial we view the time evolution of the pH. To do so go to "Results > Time evolution" yielding the following screen:

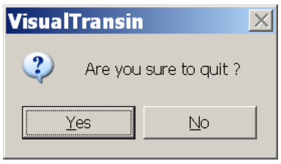


To view the pH evolution at a certain node, choose "pH" from the drop-dawn "Data type" and a node number from the drop-dawn "Node". This will give the following screen.



5.11. End

To end VGUM go to "File > Exit". The program wants to know whether we really want to end (answer yes).



The data are continuously being saved in the file "test.vtr". So no saving was required during this tutorial.

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